

# LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS

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### **Local Level**

Blackstone Fire Department, MA  
Blackstone Emergency Management, MA  
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Everett Fire Department, MA  
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Providence Fire Department, RI  
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## ***Executive Summary***

In the last ten years, the production of ethanol has increased dramatically due to the demand for ethanol-blend fuels. Current production (2010) in the United States is 13 billion gallons. Denatured ethanol (approximately 95% ethanol, 5% gasoline) is largely shipped from production facilities by rail and is now the largest volume hazardous material shipped by rail.

Large volumes of ethanol are commonly shipped by unit trains, up to 3.2 million gallons, and the larger barges can transport up to 2.5 million gallons. In Massachusetts, two to three ethanol unit trains currently travel through the state per week, as well as an ethanol barge per week. The number of trains and barges transporting denatured ethanol (95% - 98% ethanol) through the state are anticipated to increase in the future, especially if the use of higher ethanol blends becomes more prevalent. The high volume of ethanol transported and the differences in the chemical properties, and the fate and transport of ethanol as compared to standard gasoline, led to the need for additional consideration of spill response actions. In particular, this document considers the assessment and response actions for rail and barge spills of denatured ethanol.

Ethanol is a flammable colorless liquid; a polar solvent that is completely miscible in water. It is heavier than air, and has a wider flammable range than gasoline, with a Lower Explosive Limit (LEL) to an Upper Explosive Limit (UEL) range of 3.3% to 19%. The flash point for pure ethanol is 55°F, and for denatured ethanol it is much lower (-5°F). Ethanol is still considered a flammable liquid in solutions as dilute as 20%, with a flash point of 97°F. At colder temperatures (below about 51°F), the vapor pressure of ethanol is outside the flammable range. Denatured ethanol is shipped with a flammable liquids placard and North American 1987 designation.

A number of large volume ethanol incidents have occurred. Some of these have resulted in significant fires, most of which have been allowed to burn. Water has been used in some incidents, primarily to protect nearby structures or tanks. Alcohol-resistant foam has also been used, primarily to extinguish fires within tanker cars. Sampling and analysis of environmental media that has occurred in connection with spill response activities have shown impacts related to these spills, although they are generally of relatively short duration. The most significant documented impact was a large fish kill that occurred in Kentucky as a result of a bourbon spill. This effect was related to oxygen deficiency resulting from ethanol biodegradation, rather than direct toxicity. Another fish kill was observed subsequent to a spill in Illinois, but it has not been definitively attributed to the spill.

In general, ethanol in the environment degrades rapidly. Biodegradation is rapid in soil, groundwater and surface water, with predicted half lives ranging from 0.1 to 10 days. Ethanol will completely dissolve in water, and once in solution, volatilization and adsorption are not likely to be significant transport pathways in soil/groundwater or surface water. Once oxygen is

depleted as a result of aerobic degradation, anaerobic biodegradation of ethanol in groundwater results in the production of methane, which can result in an explosion hazard upon accumulating in a confined space. For an ethanol spill in typical aerobic environments, the depletion of oxygen and production of methane may take several months. Several case studies of significant spills have shown that ethanol has been completely degraded in groundwater within two to three years. The presence of ethanol can reduce the rate of biodegradation of gasoline constituents (benzene, toluene, ethylbenzene, and xylenes – BTEX) in groundwater, and thus potentially increase the persistence and dimensions of BTEX plumes. However, there is contradictory evidence that suggests that ethanol may actually enhance the rate of benzene biodegradation. Biodegradation of ethanol in surface water can result in complete depletion of dissolved oxygen, as evidenced by the fish kill documented in Kentucky.

One of the greatest hazards of ethanol is its flammability. Ethanol can conduct electricity, so electrocution hazards and possible ignition hazards are present during transloading operations.

Human exposure to ethanol during spill situations could occur by inhalation, contact with the skin, or ingestion if ethanol reaches water supplies (surface water intakes or groundwater). The odor threshold for ethanol is 100 ppm in air. No significant acute effects have been observed upon exposure to ethanol in air at 1000 ppm, and this is the OSHA Permissible Exposure Level. Effects have been observed from concentrations in air ranging from 3000 ppm to 10,000 ppm, including headaches, and eye and respiratory system irritation. Acute ingestion doses of 0.1 to 0.5 g/kg body weight are considered the threshold for central nervous system effects. Chronic effects associated with ethanol exposure are well documented, primarily associated with alcohol abuse. A dose of 0.2 g/kg body weight/day is considered the threshold for neurological effects in fetuses, and liver effects are observed at doses of 2 g/kg/day. In addition, the consumption of both alcoholic beverages and ethanol have been identified as carcinogenic in humans by the World Health Organization. However, chronic exposures to ethanol are unlikely to occur as a result of a spill, due to the rapid biodegradation of ethanol and the monitoring associated with a typical spill incident.

Water quality benchmarks (for the protection of aquatic life) have been developed: 63 mg/L for the protection against chronic effects, and 564 mg/L for acute effects. However, modeling has suggested that oxygen depletion can occur at lower concentrations. This is supported by the Kentucky spill, where the fish kill was attributed to oxygen depletion, rather than direct toxicity.

The occupational exposure limit for ethanol is 1000 ppm in air (general industry), and the concentration deemed to be Immediately Dangerous to Life or Health (IDLH) is 3300 ppm, which is 10% of the LEL. Self-contained breathing apparatus (SCBA) is necessary for spill response. For large spills with fire, evacuation of about ½ mile in all directions should be considered.



Methods for assessment and analysis of ethanol are somewhat limited due to its high solubility. A simple open flame test can be used to determine the presence of ethanol at relatively high concentrations. A hydrometer can be used to determine approximate concentrations of ethanol in water. The best option for screening is a portable Fourier Transform Infrared (FT-IR) spectrometer that has relatively low detection limits and can specify ethanol. A relatively recent analytical method (SW-846 8261) has been developed that provides low detection limits for ethanol.

Consideration of past ethanol incidents provides some insight into fate and transport in a spill situation, as well as response activities that have been effective. Consideration of these incidents, as well as conducted and possible response actions leads to the following conclusions:

- In some cases, ethanol rail incidents result in fire. In many cases, these fires have been significant, involving multiple rail cars and large volumes of ethanol;
- First responders generally have been local fire fighters that have focused on necessary evacuations, containing the fire, and protecting nearby structures and/or tanks;
- In most cases, if not all, ethanol fires have been allowed to burn, although most have not occurred in highly populated areas. Cooling water has been used to protect structures, tanks, and uninvolved rail cars;
- In some cases, where large amounts of water usage were necessary, run-off to nearby streams occurred. In one case, the stream was subsequently dammed, and 500,000 gallons of impacted water were removed for disposal;
- Alcohol resistant foam (AR-AFFF) has had limited use in these large spill and fire situations, probably due to the limited volume generally available to local fire-fighters and concerns with migration and/or recovery of the foam/ethanol. Most use has been to extinguish specific breached and burning cars that were blocking passage, or to extinguish fires inside tankers prior to removal of the contents and movement of the tanker. The use of AR-AFFF has been effective in these circumstances;
- The fires have consumed large volumes of ethanol, thus limiting impacts to environmental media;
- The most significant impacts related to ethanol spills have been to surface water. In some cases, surface water impacts have resulted in fish kills several days after the spill as a result of oxygen depletion. These impacts have occurred some distance from the site of the original spill;

- Due to concerns of surface water impacts, response activities have more recently involved efforts to prevent discharge to surface water through damming. Aeration of small creeks and large rivers has also been used to improve dissolved oxygen content; and
- Migration of spilled ethanol from the surface through soil to groundwater is also of concern, due to possible groundwater contamination and discharge to surface water, as well as methane generation. Where possible, spilled material has been recovered by pumping. In some cases, spilled material was not identified, and migration to groundwater and surface water occurred. In cases where groundwater impacts have occurred, ethanol has degraded relatively rapidly, although gasoline constituents have been more persistent.

As a result of the above observations, the following recommendations can be made:

- Contained burning is an effective response to an ethanol spill incident. It has been used in numerous spill incidents, albeit they have not generally occurred in highly populated areas;
- The use of cooling water may be necessary to protect structures, tanks, or uninvolved rail cars. Runoff from water use should be contained and/or recovered to the extent possible to prevent infiltration to groundwater and impacts to surface water;
- The local fire department stocks of alcohol resistant foam could be increased, as its use is effective. When used where the ethanol/foam can be recovered, environmental impacts will be limited. Foam not recovered and reaching surface water can increase the biochemical oxygen demand loading to streams. In addition, foam use on unpaved surfaces does not limit the migration of ethanol to groundwater;
- Ethanol pools or impacts to soils should be identified as quickly as possible to prevent infiltration to groundwater and runoff to surface water. The high solubility of ethanol can result in rapid transport in these media. Recovery and excavation have largely been used to address such situations. Controlled burn has not been used, but could be considered in some situations;
- Ethanol impacts to surface water are a significant concern. Ethanol spills reaching ditches or small creeks can be addressed by damming, thus allowing time for biodegradation and preventing releases to larger water bodies. Aeration of these smaller water bodies can be used to improve their dissolved oxygen content and enhance biodegradation, but these actions may not reduce ethanol content sufficiently prior to discharge to a large water body;



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- Once ethanol is discharged to a larger river, response options are limited. Monitoring of both dissolved oxygen and ethanol should be conducted in order to determine whether concentrations are approaching anoxic or toxic levels. Barge aerators can be used to improve dissolved oxygen levels; and
- Ethanol incidents in the marine environment have been rare, with none of a significant volume occurring in harbors or near-shore areas. Response options in such cases are similarly limited to the use of aeration to improve dissolved oxygen levels, although this would only be effective in smaller areas, such as inlets.



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## **1.0 Introduction**

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### **1.1 Objectives**

In the last ten years the production of ethanol has increased dramatically due to the demand for ethanol-blend fuels. The US currently has 204 biorefineries in 29 states, and produced more than 13 billion gallons of ethanol in 2010 (Dinneen, 2011). This is up from 10.6 billion gallons in 2009 (RFA, 2011).

In 2009, 75% of the nation's gasoline was blended with gasoline as 10% ethanol and 90% gasoline (E10). Denatured ethanol is largely shipped from production facilities by rail (70%), and is now the #1 hazardous material transported by rail (Rudolph, 2009). As a result of this increased production and transportation, several ethanol incidents have occurred in the United States since 2000, including 26 significant fires, 5 train derailments, and 3 ethanol tank fires (Rudner, 2009).

As a result of concerns related to the increased prevalence of rail transport of ethanol, and the potential magnitude of spills, the Massachusetts Department of Environmental Protection (MassDEP) requested that Shaw's Environmental and Infrastructure Group (Shaw) prepare a document containing information on the environmental impacts of and emergency response techniques for ethanol and ethanol blends. Shaw, in consultation with MassDEP, and with information provided by Ohio DEP, Illinois DEP, and Pennsylvania DEP, assembled the best information, research, and field techniques available. The anticipated users of this document are local, state, and federal responders.

### **1.2 Scope of Document**

As discussed above, ethanol is the largest volume hazardous material transported by rail. The primary mode of ethanol transport is rail. In many cases, denatured ethanol is being transported in large (80 to 100 cars) unit trains, throughout the U.S., including the northeast. Such a unit train can transport up to 2,900,000 gallons of ethanol (approximately 29,000 gallons per rail car). About 10% of ethanol is transported by barge, typically in 630,000 gallon tanker barges; although a large petroleum 2-barge unit tow can transport 2.52 million gallons. Tanker trucks (about 8000 gallons) are also used to transport ethanol, although primarily ethanol blends (USDA, 2007).

This document focuses on larger volume releases of denatured ethanol or ethanol blends during transportation by rail or barge. In Massachusetts, it is estimated that there are 2-3 ethanol unit trains traversing the state per week, as well as an ethanol barge every other day. This document does not specifically address releases during production, storage, transfer, or during smaller

volume transport by highway cargo tankers, although much of the information presented is also relevant to these types of releases.

Table 1-1 shows the most common ethanol blends and their uses. There are also mid-level blends (20%, 30% and 40% by volume), although these are less common than those shown below. As shown in the table, the ethanol blends are commonly referred to as E-blends, with the numbers indicating the percentage of ethanol in the blend.

TABLE 1-1 ETHANOL AND BLENDS AND THEIR USES		
Ethanol Blend	Composition	Use
E100	100% ethanol, also known as neat ethanol or fuel grade ethanol	Used in the production of blends, not generally transported in large quantities
E95 – E99	95% - 99% ethanol, balance gasoline, also known as denatured ethanol	Transported in large quantities to bulk terminals for production of general use blends
E85	85% ethanol, 15 % gasoline	Used in flex-fuel vehicles (< 2% ethanol consumed for this use)
E10	10% ethanol, 90% gasoline	70 % of nation's gasoline (98% ethanol consumed for this use)

This document provides the following information:

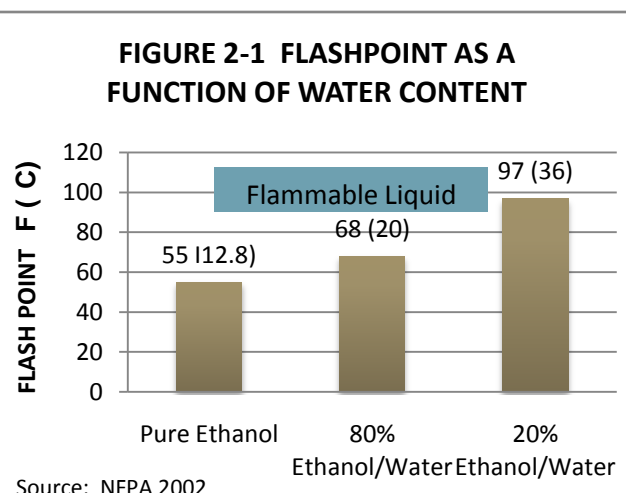
- Physical and chemical characteristics of ethanol and blends (Section 2.0);
- Summary of case studies of incidents involving ethanol (Section 3.0);
- Fate and transport characteristics of ethanol and blends (Section 4.0);
- Health effects and environmental risks associated with ethanol and blends (Section 5.0);
- Spill assessment and delineation, including screening and analytical methods (Section 6.0);
- Response options for ethanol spills by environmental medium (Section 7.0); and
- Summary and recommendations (Section 8.0).

## 2.0 Physical and Chemical Characteristics of Ethanol/Gasoline Blends

### 2.1 Physical/Chemical Properties

Ethanol is a flammable colorless liquid. It is a polar solvent that is volatile and completely miscible (mixes) in water. Vapors of ethanol are characterized as having a vinous or wine-like odor (HSDB, 2011). Table 2-1 shows the chemical/physical properties of ethanol. The vapor density of 1.59 indicates that it is heavier than air and will seek lower altitudes (tend to collect closer to the floor level) (IFCA, 2008). Its specific gravity indicates that it is lighter than water, but it will thoroughly mix with water. Once mixed, it will not separate. It has a wider flammable range than gasoline, has a blue flame, and does not produce visible smoke (IFCA, 2008) unless denatured with gasoline.

The flammability of ethanol is affected by mixture with water, but remains flammable even with the presence of 80% water, as shown in Figure 2-1. At this concentration, the flash point is 97°F (36°C), and it is still considered a flammable liquid. The flash point is the lowest temperature at which vapor formed above liquid



**TABLE 2-1 CHEMICAL/PHYSICAL PROPERTIES OF PURE ETHANOL**

Formula	•C <sub>2</sub> H <sub>6</sub> O
Molecular Weight	•46.07
Color/Form	•Clear, colorless, very mobile liquid
Odor	•Mild, like wine or whiskey (vinous)
Ionization potential	•10.47eV
Boiling Point	•173 F (78.5 C)
Melting Point	•-173 F (-114 C)
Liquid Density	•0.79 at 20 C
Vapor Density	•1.59
Flammable Range	•3.3 - 19%
Solubility	•Miscible in water and organic solvents
Vapor Pressure	•59.3 mm Hg at 25 C
Flash Point	•55 F (13 C)

Source: HSDB 2011

ignites in air at standard pressure (1 atmosphere). This is not the same as the temperature at which combustion will continue. This is known as the fire point, or the lowest temperature at which heating beyond the flash point will support combustion for 5 seconds. This characteristic is not commonly measured, and no information on the fire point of ethanol was found.

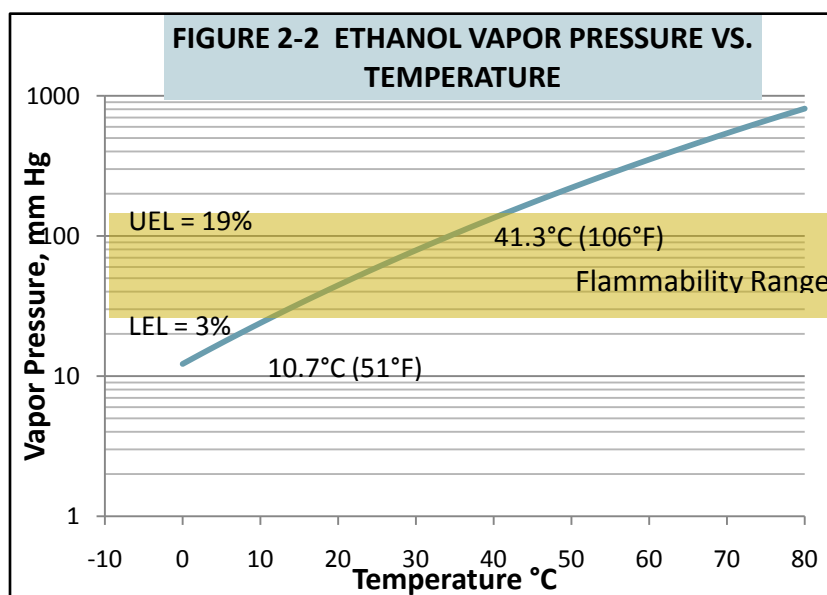
Ethanol blends will have properties affected by the percentage of ethanol in the blend. A comparison of some of the relevant properties is found in Table 2-2. This table shows the flash point for both ethanol and gasoline. As shown in Table 2-2, once gasoline is added to ethanol for denaturing (E95), the flashpoint decreases dramatically from 55°F to -5°F. The flash point continues to decline with a greater content of gasoline.

**TABLE 2-2 COMPARISON OF PROPERTIES FOR ETHANOL/GASOLINE BLENDS**

PROPERTY	ETHANOL	E95	E85	E10	Gasoline
Flammable Range	3.3%-19%	3.3%-19%	1.4%-19%	1.4%-7.6%	1.4%-7.6%
Flash Point	55°F (12.8°C)	-5°F (-20°C)	-20°F -5°F (-29°C - -20°C)	-45°F (-43°C)	-45°F (-43°C)

Source: HSDB (2011), Speedway (2004), NRT (2010), IFCA 2009

Properties are also affected by temperature. Figure 2-2 shows the vapor pressure of ethanol as it varies with temperature. This figure also shows the flammability range at standard pressure. As

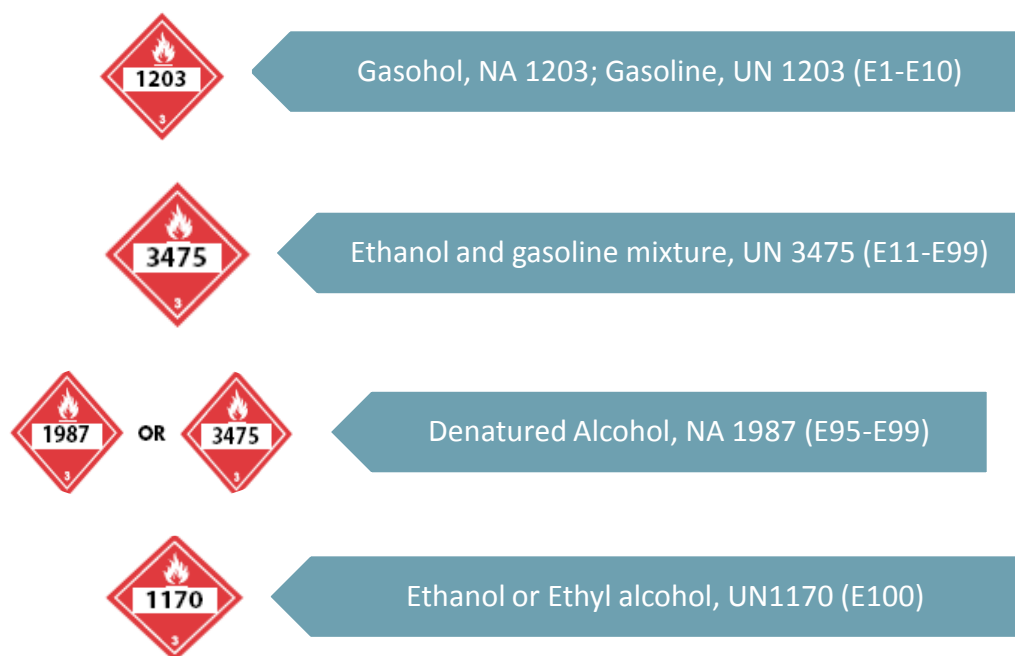


shown in Figure 2-2, at colder temperatures (below 10.7°C (51°F), the vapor pressure of ethanol is outside the flammable range. As discussed above, the addition of gasoline would change this graph, decreasing the temperature at which, for example, E95 would be outside the flammable range.



## 2.2 DOT Placards

DOT (2008) issued new and revised shipping names and identification numbers (ID) to be used for fuel mixtures of ethanol and gasoline in 2008. The proper shipping names, labels, and identification numbers are shown below:





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### 3.0 Summary of Case Studies

Although ethanol has been produced and transported in large volumes for several decades there have been relatively few incidences involving its catastrophic release into the environment. There have been several occasions of leaking of underground storage tanks containing ethanol fuel blends, some for very long periods. These have involved E-10 type fuels which are not the focus of this report.

Most of the high-concentration ethanol is moved from production plants to blending terminals by rail. Consequently, the majority of the event data is from rail incidents, several of which will be discussed in detail in Appendix A. The other well-documented sources of ethanol impact to the environment have been the result of fire incidents at distilleries. Two very significant events occurred in Kentucky in 1996 and 2000. There have been few marine incidents. Some of the more significant incidents that have occurred involving ethanol are summarized in Table 3-1. More detail is presented in Appendix A.

**TABLE 3-1 ETHANOL SPILL INCIDENT SUMMARIES**

Description	Volume	Comments
Railroad Incidents		
<b>2006-New Brighton, PA</b>  Derailment of 23 30,000 gallon railcars containing denatured ethanol along a bridge crossing the Beaver River	Approximately 600,000 gallons either burned or released with an estimated 60,000 gallons into Beaver River	<ul style="list-style-type: none"> <li>Fire allowed to burn itself out over a few days</li> <li>Three cars were in the river, but were not compromised</li> <li>Beaver River is large and fast-flowing no detrimental impacts noted</li> <li>Removal of limited impacted soil and ballast performed</li> </ul>
<b>2007-Painesville, OH</b>  Derailment of 30 cars including five 30,000 gallon cars containing denatured ethanol. Additional involved cars of phthalic anhydride, bio-diesel, and butane	150,000 gallons either spilled or burned	<ul style="list-style-type: none"> <li>Fires controlled and allowed to burn</li> <li>Presence of other more flammable materials caused fire-fighters to use copious amounts of water</li> <li>Two streams impacted. 500K gallons of water/chemicals removed from one, aerators used in the other</li> <li>Visibly impacted soils excavated</li> </ul>
<b>2008 Luther, OK</b>  Derailment of seven 30K cars containing ethanol and crude oil.	Up to 210,000 gallons of ethanol/crude oil	<ul style="list-style-type: none"> <li>Fire allowed to burn itself out</li> <li>Limited visible impact, site not near water</li> </ul>
<b>2009-Knoxville, TN</b>  Derailment of five 30K gallon cars with ethanol	6000 gallons spilled	<ul style="list-style-type: none"> <li>Cars flipped but did not explode or burn</li> <li>Estimated 6000 gallons missing from two leaking cars when up righted</li> <li>Approximately 1000 gallons collected from ground surface</li> <li>Occurred in paved area with little soil and no surface water nearby</li> </ul>

**TABLE 3-1 ETHANOL SPILL INCIDENT SUMMARIES (continued)**

Description	Volume	Comments
2009-Rockford, IL  Derailment of fourteen 30K gallon cars of denatured ethanol.	Estimated 360,000 gallons burned, 75,000 gallons spilled	<ul style="list-style-type: none"> <li>One motorist killed and nine injured</li> <li>Massive fire required evacuation of 600 homes</li> <li>Fire allowed to burn for 24-hours</li> <li>About 1400 tons soil and 57,000 gallons ethanol removed from site</li> <li>Fish kill observed in Rock River, but has not been definitely related to spill</li> <li>Sampling of air, soil, surface water, groundwater, private wells, and fish showed no significant impacts to air, water, or soil; ethanol and acetaldehyde detected in fish</li> </ul>
2010 – Bryan, OH  Derailment of 37 cars, some of which contained ethanol	80,000 gallons spilled	<ul style="list-style-type: none"> <li>No fire resulted</li> <li>Impact to waterway</li> <li>Monitored using dissolved oxygen and biochemical oxygen demand</li> <li>Restoration of dissolved oxygen in surface water took several months</li> </ul>
2011-Arcadia, OH  Derailment and burning of thirty-one 30K gallon cars of denatured ethanol. A total of 23 cars involved in fire and/or compromised	Estimated 680,000 gallons burned or spilled	<ul style="list-style-type: none"> <li>Massive fire allowed to burn for several days</li> <li>Foam used inside tankers prior to pumping them off</li> <li>ethanol/water entered a nearby creek and field drainage system</li> <li>Over 800,000 gallons of fuel/water mix removed, with collection ongoing</li> </ul>
Distillery Events		
1996-Bardstown, KY  Seven bourbon storage/aging warehouses and thirteen distillery structures	5.6MM gallons of 107-112 proof (54-56% alcohol) bourbon burned or spilled	<ul style="list-style-type: none"> <li>High winds created massive fire that was controlled and allowed to burn out</li> <li>Spilled liquids pooled and burned, burn footprint was within paved area</li> <li>No impact to surface water</li> </ul>
2000-Lawrenceburg, KY  One bourbon storage/aging warehouse	980,000 gallons of 107-112 proof bourbon	<ul style="list-style-type: none"> <li>Building located above Kentucky River, fire allowed to burn out</li> <li>Liquid travelled down a hill into river below</li> <li>After 2 days fish kill occurred, became the largest in KY history</li> <li>Fisk kill due to depleted dissolve oxygen; area of “dead water” stretched 7 miles</li> <li>Barges used to aerate the water for 4 days until dissolved oxygen levels were restored</li> </ul>
Maritime Events		
2004-50 miles off VA coast  Tanker ship at sea	3.5MM gallons of ethanol on-board	<ul style="list-style-type: none"> <li>Explosion on board caused by vapors from empty tanks that had previously contained MTBE</li> <li>Ship lost 3-dead, 18 crew missing 6-survivors</li> <li>Ethanol cargo lost, no environmental damage reported</li> <li>All environmental damage related to 49K gallons of fuel oil lost</li> </ul>
2010-New York Harbor  Tanker ship-ruptured tank	Cargo tank ruptured while taking on 55K barrels of ethanol	<ul style="list-style-type: none"> <li>No release to water</li> <li>Rupture from over-filling</li> <li>Rupture caused deck collapse</li> </ul>

## 4.0 Fate and Transport Characteristics

This section provides information regarding the fate and transport of ethanol in various environmental media, including soil, ground water, surface water and air. Information is provided here in summary form, with further detail included in Appendix B.

Ethanol may be released to the environment as pure (also referred to as neat) ethanol or a blend with various percentages of gasoline and ethanol (also referred to as an E-blend fuel). Accidents that occur during large volume transport of ethanol via rail cars and marine tankers or as a result of structural failure at ethanol bulk storage terminal terminals are possible sources of the release of neat or denatured ethanol. Tanker truck accidents, splash blending of ethanol with gasoline, and leaks and spills at retail and non-retail gasoline stations may release moderate to small volume E-blend fuels into the environment. The release of neat or denatured ethanol into the environment results in fate and transport issues that can be different than those from an E-blend release, as shown in Table 4-1.

**TABLE 4-1 COMPARISON OF FATE AND TRANSPORT OF NEAT ETHANOL WITH E-BLENDS**  
Source: NEIWPCC, 2001

Characteristic	Neat Ethanol, E95 or Denatured Ethanol	E-Blends (E85 and lower)
<b>Release Type</b>	Large volume, surface soil and water spill	Moderate to small volume, surface or subsurface spill
<b>Release Source</b>	Rail cars, marine tankers, bulk storage terminals	Trucks, retail gas and blending stations
<b>Transport Paths</b>	Surface spreading until reaching surface water body; soil infiltration and leaching to groundwater	Nominal surface spreading, followed by soil infiltration and leaching to groundwater
<b>Media affected</b>	Soil, groundwater, lakes, wetlands, rivers, harbors, shorelines, and sewers. Explosion potential if large volumes flow in confined spaces such as sewers.	Primarily soil and groundwater. Localized impacts to lakes, wetlands, rivers and sewers if located immediately adjacent to accident site.
<b>Environmental fate</b>	Rapid biodegradation of ethanol in soil or groundwater. There are multiple variables and uncertainty associated with predicting degradation and extent of migration after surface spill.	Rapid biodegradation of ethanol in soil or groundwater, more predictable rates
<b>Co-solvency of other gasoline components</b>	Co-solvency not prominent at uncontaminated locations. When neat ethanol is released into a soil where gasoline contamination has already occurred (such as bulk terminals) the mobility of gasoline can be increased.	Ethanol may extend the length of benzene plume in groundwater due to co-solvency of gasoline components in ethanol and reduced natural attenuation of benzene

Some important fate characteristics of ethanol are described below – migration pathways, degradation rates, methane generation, and partitioning. This discussion is followed by a discussion of fate and transport characteristics by environmental medium.

## 4.1 Ethanol Migration Pathways

In evaluating the potential impact of an ethanol release to the environment, it is essential to take into account the pathways that ethanol could travel from the release point. The major migration pathways include the following:

- Infiltration into soil
- Transport in groundwater
- Surface release/runoff to streams, fast and slow flowing rivers, lakes, coastal water areas, outer harbors, open water, ditches, wetlands and storm/ sanitary sewers
- Dispersion into air

Table 4-2 presents a summary of the fate of ethanol as it migrates through each of these environments. Ethanol concentrations are reduced rapidly at rates that depend upon the migration pathway, as well as the environmental characteristics, such as temperature, soil type, flow rate, etc. While degradation rates are rapid, there is still a possibility of rebound if a source is still present.

**TABLE 4-2 FATE OF ETHANOL AFTER MAJOR RELEASE**

<b>Soil</b>	<ul style="list-style-type: none"> <li>• Ethanol is rapidly biodegraded in soil</li> </ul>
<b>Surface Water</b>	<ul style="list-style-type: none"> <li>• Neat ethanol rapidly mixes with water</li> <li>• E-blend will mix with water, but in large volume water bodies, ethanol will separate from the gasoline.</li> <li>• Ethanol is rapidly biodegraded in surface water</li> </ul>
<b>Groundwater</b>	<ul style="list-style-type: none"> <li>• Ethanol is rapidly biodegraded in groundwater</li> <li>• Ethanol release may induce the transport of other chemicals such as benzene</li> </ul>
<b>Air</b>	<ul style="list-style-type: none"> <li>• Ethanol vapor is denser than air and tends to settle in low areas.</li> <li>• Ethanol vapor disperses rapidly after release.</li> </ul>
<b>Storm / sanitary sewers</b>	<ul style="list-style-type: none"> <li>• Ethanol will volatilize and rapidly biodegrade.</li> <li>• The potential decrease in dissolved oxygen as a result of ethanol degradation can upset microbial functions at wastewater treatment plants.</li> <li>• The potential flammability hazard must be addressed when ethanol is released to a sanitary or storm system.</li> </ul>

Source: EPA 2009

## 4.2 Ethanol Degradation Rates

In the atmosphere, it is predicted that ethanol will be oxidized quickly; with half-lives between 0.5 and 5 days. In soil and groundwater, ethanol undergoes rapid biodegradation with a half-life ranging from 0.1 to 2.1 days, although more recent studies indicate that the half-lives may be

larger (5 to 10 days). In surface water following a pure ethanol spill, ethanol is predicted to quickly biodegrade with half-lives ranging from 0.25 to 1 day. Due to rapid loss of ethanol through photo-oxidation in air and biodegradation in soil and water, ethanol is unlikely to accumulate in the soil, air, surface water, or groundwater. This is consistent with reports of monitoring results from spill situations (see Section 3.0 and Appendix A). There is a great deal of uncertainty as to how these estimated rates of ethanol loss (and other literature values) will apply in realistic field conditions. Therefore, these rates represent generic order-of-magnitude estimates and may not be applicable for site-specific releases.

### **4.3 Methane Generation in Soil/Groundwater**

Anaerobic biodegradation of ethanol in groundwater results in the production of methane. The presence of methane in the unsaturated soil in excess of the explosive limits may present an explosion hazard. Methane vapors can be produced over an extended period of time and persist in soil gas for a long time, at levels exceeding the lower and upper explosive limits for methane (3.3% and 19% by volume, respectively). This process is discussed in more detail in Section 4.5.1 and 4.5.2 below and Appendix B.

### **4.4 Ethanol Partitioning Between Environmental Media**

The partitioning of ethanol mass between air, water, and soil media is summarized below. More detail is presented in Appendix B.

- *Air/Water Partitioning:* Ethanol has a tendency to remain in the aqueous (liquid) state. Therefore, atmospheric ethanol is likely to partition into water vapor droplets. Ethanol in surface water and groundwater is likely to remain in the aqueous phase. As a result, ethanol volatilization from surface water or off-gassing from groundwater are not likely to be significant mechanisms for ethanol mass loss from water.
- *Soil/Water Partitioning:* Ethanol is not strongly adsorbed to soil particles, and is likely to migrate at the velocity of the groundwater. Adsorption to aquifer materials in the subsurface or to sediments in surface water is not likely to affect the fate of ethanol in the environment.

### **4.5 Media Fate and Transport Characteristics**

#### **4.5.1 Soil**

Ethanol and E-blend fuel spilled on land surface will infiltrate the soil, and the ethanol and gasoline components of the E-blend fuel will slowly infiltrate down through the pores of the soil until they reach the top of the water table. Ethanol has a higher mobility through the soil as

compared to other gasoline components because it does not preferentially adsorb to the soil grains.

During the process of infiltration through soil, a fraction of ethanol and gasoline components are retained in the pores (soil vapor or soil moisture) or adsorbed to soil grains. The fraction that is not retained in the unsaturated soil will reach groundwater. As discussed above, ethanol tends to partition to the water phase (soil moisture) in preference to the air in the soil pores or adsorption to the soil grains. The fraction of ethanol retained in the unsaturated zone depends greatly on the volume of soil impacted by the release, the water content of the soil, and the rate at which gasoline infiltrates through the subsurface. The fraction of ethanol that infiltrates to groundwater goes into solution because of high water solubility of ethanol. The gasoline component of the E-blend fuel floats on water because it is less dense than water, however these constituents will also dissolve and migrate downward.

For E-blend spills, the presence of ethanol results in gasoline hydrocarbons being able to enter smaller pore spaces and drain more easily from unsaturated soils into the groundwater. Therefore, the presence of ethanol can result in mobilizing existing soil contamination.

As discussed earlier, ethanol has a short half life in soil. Therefore, ethanol present in soil vapor or soil moisture will rapidly biodegrade. Some volatilization from moist soil surfaces is expected although the majority of ethanol is expected to be retained in the soil moisture and be lost through the process of biodegradation. In dry soils, some volatilization is expected to occur (HSDB, 2011).

Neat ethanol releases at distribution terminals can affect the behavior of previously released fuel hydrocarbons in the following ways:

- Ethanol dissolves and mobilizes light non aqueous phase liquid (LNAPL) that was previously entrapped in the unsaturated and saturated zones.
- Ethanol creates a capillary fringe depression on top of the water table into which all nearby LNAPL can drain.

As discussed in Section 4.3 and Appendix B, anaerobic biodegradation of ethanol in groundwater results in the production of methane. Methane generation typically will not occur until available electron acceptors (i.e., oxygen, nitrate, iron, and sulfate) are consumed. Laboratory studies indicate that it took 6 to 10 weeks for conditions to be suitable for the generation of methane. Actual times after a spill until methane is generated will depend on the presence of oxygen and other electron acceptors, the temperature, the soil type, the presence of



other alcohols or hydrocarbons, the groundwater flow rate, and other site-specific characteristics. One study of a neat ethanol spill indicated that methane was present in groundwater 15 months after the spill occurred, and concentrations began to increase dramatically within 3 to 8 months of that time. From these field observations and the laboratory studies, it can be concluded that methane generation will generally not start for several months in an environment that is initially under aerobic conditions. Once methane is present in groundwater, it will volatilize from groundwater into soil gas. In the field study described above, a methane survey taken 23 months after the spill showed methane concentrations in soil gas above the LEL at a depth of 4 feet below the ground surface. This could pose a hazard for construction or monitoring activities in a spill area, and if the methane in soil gas were to migrate to a confined space, it may lead to an explosion hazard.

After an ethanol spill, the following conditions must be met for an explosion hazard to occur from methane:

- **Methane gas generation.** Degradation of ethanol to methane is expected to be the dominant degradation pathway in soil/groundwater. The presence of methane in the unsaturated soil in excess of the explosive limits may present an explosion hazard;
- **Methane gas migration.** Migration of methane gas from soil and groundwater to underground utility pipes, drains, conduits or through natural or man-made subsurface preferential migration pathways; and
- **Collection in a confined space.** Collection of methane gas in a confined space to a concentration at which it could potentially explode, such as a manhole, a subsurface space, a utility room in a home, or a basement. For methane, the LEL is 3.3% by volume and the UEL is 19% by volume. At concentrations below its LEL and above its UEL, a gas is not considered explosive.

Methane vapors can be produced over an extended period of time and persist in soil gas for a long time at levels that could pose an explosion hazard.

#### **4.5.2 Groundwater**

Like other alcohols, ethanol is hydrophilic (attracted to and soluble in water) whereas standard gasoline is hydrophobic (repelled by water). Ethanol partitions preferentially into the aqueous phase. Ethanol is completely miscible in both gasoline and water at all concentrations. The presence of ethanol, therefore, affects the fate and transport mechanisms of E-blend fuels. In presence of ethanol, the behaviors of water and gasoline are modified as follows:

- Solubility of gasoline hydrocarbons in water increase;
- Solubility of water in gasoline increases; and
- Interfacial tension between the water and the gasoline phases is reduced.

The release of ethanol can impact groundwater after infiltrating through the soil. An ethanol plume in groundwater may result, depending upon the volume of ethanol spilled on the surface, the thickness of the unsaturated soil column (depth to groundwater), and the conductivity of the soil. Once ethanol reaches the groundwater, it will dissolve and disperse rapidly.

Ethanol tends to dissolve completely into the groundwater and move with the groundwater in the direction of groundwater flow. In case of E-blend fuels, the soluble components of gasoline that include benzene, toluene, ethylbenzene and xylenes (BTEX) will partially dissolve, while ethanol will dissolve completely. Unlike the gasoline components, ethanol does not adsorb to the saturated soil and therefore moves with groundwater faster than the BTEX components. The BTEX components of E-blend fuels adsorb to soil particles and later desorb to become dissolved again in the groundwater, resulting in these gasoline constituents traveling at a slower rate than groundwater and ethanol. The less soluble constituents of E-blend fuels will migrate with the undissolved hydrocarbon pool.

**TABLE 4-3 EFFECT OF ETHANOL ON GASOLINE FATE AND TRANSPORT IN GROUNDWATER**

**Depletion of oxygen and nutrients**

- Inhibits the degradation of more toxic components in gasoline (e.g. BTEX)
- May make the dissolved BTEX plume longer

**Surface Tension Effect**

- Causes gasoline components to spread laterally

**Co-solvency**

- Makes other gasoline constituents more soluble

Source: HSDB, 2011

In general, the impacts of neat ethanol with respect to the contamination of groundwater are less severe compared to E-blend fuels. When neat ethanol is released into the groundwater it can be degraded rapidly by microorganisms until the necessary electron acceptors are depleted, unless the ethanol volume and concentrations are so high that they restrict microbial activity. On the other hand, an E-blend gasoline release to groundwater enhances the groundwater transport of benzene, toluene, ethylbenzene and xylenes (BTEX) in gasoline, especially benzene. The environmental effects of ethanol on the gasoline components of E-blends are summarized in Table 4-3.

The rapid biodegradation of ethanol first depletes the oxygen content of groundwater and then the anaerobic electron acceptors (e.g., nitrate, sulfate), and therefore could potentially reduce the rate of biodegradation of the BTEX constituents. The presence of ethanol in E-blend fuels can cause the BTEX compounds of gasoline to travel farther than a standard gasoline blend without ethanol. Some recent studies contradict this and suggest that ethanol may actually enhance the rate of benzene biodegradation, thereby reducing benzene plume length and persistence.

The rapid biodegradation of ethanol has a side effect on the groundwater transport. Ethanol acts as an energy source and stimulates the growth of aerobic and anaerobic microorganisms in groundwater. This may in turn result in the growth of biofilms on aquifer material, mineral precipitation and the generation of nitrogen and methane gases, processes which alter the hydraulic properties of the aquifer such as reduction in porosity and hydraulic conductivities. The rapid biodegradation of ethanol may also lead to a significant accumulation of volatile fatty acids which are potential degradation products of ethanol and that could decrease the pH to levels that inhibit further bioremediation. The rapid consumption of oxygen by ethanol means the groundwater will become anaerobic quickly. Anaerobic biodegradation of BTEX and ethanol typically occurs much more slowly than aerobic biodegradation, although the rates of anaerobic biodegradation of ethanol are still fast enough (in days) that ethanol is not expected to persist for a long duration. Empirical data from a case study of an ethanol spill at a Pacific Northwest terminal (presented in Appendix B) indicates that for most spills the ethanol in groundwater is expected to be degraded and not be of concern in a year or two. In comparison, BTEX constituents have been measured in groundwater for several years and sometimes even decades after a gasoline spill.

The enhanced anaerobic microbial activity caused by the presence of ethanol in groundwater leads to methanogenesis, which is the production of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) by biological processes. Details of the chemistry behind the methanogenesis and the volumetric estimation of methane generation from ethanol are provided in Appendix B. There is potential for ethanol-induced methane production to restrict groundwater flow and to pose an explosion hazard, as discussed in Section 4.3.

Empirical data regarding the persistence of ethanol generated methane in soil and groundwater was collected at a bulk fuel terminal in the Pacific Northwest, where 19,000 gallons of neat ethanol were accidentally released from an above ground storage tank in 1999. Further details of the spill and spill monitoring are provided in Appendix B. Over time, the ethanol plume concentrations declined and high methane concentrations were measured in the area of the ethanol plume. This empirical data suggests that methane related hazards will extend to the area occupied by the ethanol plume in groundwater, and will extend to a distance that can be

estimated from the groundwater velocity and the time since the release. The extent of the groundwater plume will provide the upper bound for the extent of methane impacts, except for any preferential pathways such as utilities that may provide further spread of the methane in soil gas.

When neat ethanol is spilled at locations where petroleum contaminated soil and groundwater plumes already exist (e.g., oil terminals), the ethanol can remobilize the gasoline components and cause lateral spreading of liquid petroleum and several fold increases in the concentration of benzene and other constituents of gasoline. This may result in contamination of groundwater and nearby water supply wells. Ethanol can also facilitate iron reduction and sulfate reduction, which can have significant impacts on groundwater quality. The potential for contamination of water wells or degradation of water supply depends on several factors, such as the volumes and the concentrations of ethanol and gasoline components at the release site, the local hydrogeological conditions, and the location of the spill relative to the area of groundwater capture for the water supply well.

#### **4.5.3 Surface Water**

Ethanol in surface water can originate from a number of sources:

1. Rainwater (through atmospheric volatilization and deposition) – minimal contributions, not further considered in this document.
2. Direct discharges from land surface (from accidental spills) – immediate and severe impacts after spill, serious threat to environment, high concentrations and volumes of ethanol expected, sudden and severe depletion of dissolved oxygen because of the biodegradation of ethanol with acute toxic effects potential such as fish kills.
3. Direct discharges from land surface to drainage features or small creeks, which may discharge to larger surface water bodies – Less severe impacts immediately after spill, but still may result in severe depletion of oxygen.
4. Marine cargo tanker / barge accidents – short term impacts after the spill, high concentrations and volumes of ethanol expected initially, impacts to near-shore coastal marine environment likely, ethanol is expected to be lost rapidly due to dilution and dispersion in marine waters. Oxygen depletion may occur in coastal areas with less flushing.
5. Contaminated groundwater plume migration to surface water – longer term, lower intensity impacts after a spill, timing and magnitude dependent on the distance of the

surface spill to the surface water body and other factors such as the degree of biodegradation and natural attenuation during transport in groundwater, the hydrogeologic settings, the hydrology of the surface water body, and the volume of the spill.

After a large volume surface spill, neat ethanol or E-blend fuel will flow over pavement and soil until reaching a point of discharge into storm sewers, wetlands, lakes, and streams. During the overland flow over soil and pavement, ethanol will partially volatilize into the atmosphere. As the ethanol flows over soil, some of the ethanol will infiltrate the soil and reach the groundwater, which may discharge to a surface water body. The remaining ethanol could reach a wetland or a surface water body directly. Upon reaching a surface water body, either as groundwater discharge or surface flow, ethanol will rapidly mix with the water and go into solution because ethanol is completely soluble in water.

Once ethanol reaches fresh water, whether it is a flowing water body such as a stream or a standing water body such as a lake or wetland, ethanol is not expected to volatilize quickly. While volatilization from water surfaces does occur, the estimated volatilization half-lives for a model river and model lake are 3 and 39 days, respectively, which are significantly larger than the biodegradation rates for ethanol in water (few hours to a day). Ethanol is also not expected to adsorb to suspended solids and sediment in the surface water bodies. Hydrolysis of ethanol and photolysis in sunlit surface waters are not expected to reduce ethanol concentrations. Ethanol is therefore expected to remain in solution in the water while biodegradation is occurring.

High concentrations of ethanol may occur in the immediate downstream area of a spill with little biodegradation, especially after a large volume spill into a surface water body. The high concentrations of ethanol would rapidly deplete the dissolved oxygen content of the fresh water bodies that have low aeration rates (e.g., lakes, ponds, lakes and large rivers with little turbulence), leading to the possibility of a fish kill from oxygen stress. As discussed in Section 3.0 and Appendix A, in May 2000, a 500,000 gallon release of Wild Turkey bourbon that contained 50% ethanol (250,000 gallons) into the Kentucky River caused the worst fish kill in 50 to 60 years. This fish kill was attributed to depletion of dissolved oxygen and not the direct effects of ethanol.

Biodegradation will begin to reduce ethanol concentration shortly after release as long as the water is warmer than 10°C (50°F). It is important to note that this temperature is approximately the same as the threshold for ethanol's flammability; at colder temperatures below 10.7°C (51°F) the vapor pressure of ethanol is outside the flammable range (see Figure 2-2). Therefore, even

though the flammability risk following an ethanol spill is reduced in cold weather, the impacts to surface water may be greater due to limited biodegradation.

Ethanol has been shown to biodegrade under aerobic and anaerobic conditions. If the temperature ranges are appropriate, the biodegradation of ethanol in surface water proceeds rapidly, with half lives ranging from hours to a day. Therefore, in warm waters ethanol is unlikely to persist for an extended time. In cooler water bodies, ethanol will mix rapidly and migrate with water without much loss except for dilution. If conditions favorable to biodegradation are not present, ethanol may persist for several months.

Large volumes of ethanol, up to 2.5 million gallons, may be released into marine waters from the rupture of a marine tanker or a barge carrying bulk ethanol. Due to the infinite solubility of ethanol in water, it will tend to distribute near the water surface because it is less dense than water. Marine ethanol spills pose a threat of being toxic to the ecological receptors in direct contact with the release and could impact the surface aquatic ecosystem. Ethanol released to the marine environment is not expected to persist for a long duration because ethanol in the surficial marine environment will be lost by the processes of dispersion and dilution as well as biodegradation, resulting in the rapid natural attenuation of the marine ethanol spills. Near-shore releases of ethanol are of greater concern to the proximity of sensitive receptors and the possibility of reduced flushing in some locations.

The salinity of the marine water is expected to have minor effects on the fate and transport of the ethanol. Environmental degradation in salt water may be slower than freshwater. For E-blend fuels, the higher salinity of marine waters will tend to further reduce the solubility of the gasoline components, ensuring that the gasoline components continue to float on water and are less readily available to marine organisms that inhabit the deeper marine environment. In some marine estuaries, the higher density salt water may form a wedge at the deeper parts of the estuary. Such a wedge tends to slow the mixing of ethanol and E-blend fuels with the deeper waters (NRT, 2010).

Another consideration in the fate and transport is the energy level of the surface water body that receives the spilled ethanol. In flowing or fast water such as rivers, streams, marine environment with breaking surf, the high mixing energy of the receiving water body will result in rapid mixing of ethanol with the entire water column. Ethanol concentrations will decrease due to rapid dilution and also due to the high aeration rates as compared to still water bodies like ponds and lakes (NRT, 2010)

#### **4.5.4 Air/Vapor**

If released to the atmosphere, ethanol disperses rapidly in the vapor phase. Ethanol vapor is denser than air, and will eventually settle in low lying areas. If there is moisture in the atmosphere, the atmospheric ethanol is likely to partition into water vapor droplets. Ethanol in surface water and groundwater is likely to remain in the aqueous phase and degrade at a rate that is faster than the rate of volatilization. As a result, ethanol volatilization from surface water or off-gassing from groundwater are not likely to be significant contributors to ethanol in the atmosphere.

In the atmosphere, the half life of ethanol is similar to that of other alkyl ether oxygenates, including methyl tertiary-butyl ether (MTBE). Vapor phase ethanol is degraded in the atmosphere by reaction with photo chemically-produced hydroxyl radicals, and in summer conditions, half-lives are on the order of days.

Ethanol can impact the air quality and lead to a safety hazard. Some examples are as follows:

- Noxious odors may be produced by the generation of butyrate, a metabolite of ethanol biodegradation;
- Ethanol vapor has the potential for formation of explosive mixtures. Ethanol surface flow into a confined space, such as a storm sewer, may create an explosive situation when vapors of the ethanol collect in air pockets in the sewer;
- Anaerobic biodegradation of ethanol in groundwater produces methane. At higher concentrations (near 1000 mg/L) ethanol rapidly ferments to methane at a rate near 20 to 60 mg/L per day. Methane leaves the ground water and enters soil gas where it can present an explosion hazard if it enters a confined space, as discussed previously; and
- The methane vapors are produced over an extended period of time and persist in soil gas for a long time, at levels exceeding the upper explosive limit (19% by volume).

Biodegradation of ethanol and E-blends has the potential to expedite vapor intrusion of BTEX compounds. The methane originating from the anaerobic degradation of ethanol in groundwater undergoes aerobic biodegradation in soil pores and consumes the available oxygen from the soil gas. This oxygen would otherwise be available to degrade benzene and other gasoline constituents introduced to soil gas from an E-blend spill. The aerobic degradation of benzene is therefore limited in presence of ethanol. The lack of benzene degradation caused by the consumption of oxygen by methane results in increased persistence of benzene in soil gas.



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## LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS



## **5.0 Health Effects and Environmental Risks**

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### **5.1 Environmental Risks – Fire and Explosion**

Flammability is the greatest hazard for ethanol and E-blend fuels, just like it is for gasoline. Gasoline has a fairly narrow range of flammability (between 1.4 and 7.6% or 14,000 and 76,000 ppm by volume), while ethanol has a wider range of flammability (3.3 to 19% or 33,000 to 190,000 ppm by volume). Given the concern for flammability, the level determined to be Immediately Dangerous to Life and Health (IDLH) has been set by NIOSH as 10% of the LEL, or 3300 ppm.

Ethanol is also completely water soluble unlike gasoline which floats on water. Large amounts of water are required to dilute ethanol to the point where it no longer supports combustion, as discussed in Section 2.1. If released as an E-blend fuel into water, gasoline will float on a layer of an ethanol-water solution, and the resulting ethanol water solution will still be flammable.

While smoke from burning gasoline is thick, black and toxic, pure ethanol burns without visible smoke and has a hard-to-see blue flame. In denatured (E-95) form, a slight orange flame and some smoke may be visible. Because ethanol is flammable, and burns with a virtually invisible flame, such a fire would be especially hazardous to emergency responders. Anecdotal evidence from Indy motor races suggests that the invisibility of ethanol flame is a hazard requiring the maintenance crew to use a corn broom to detect the ethanol flame, unlike gasoline fires that can be visually detected due to the smoke.

Ethanol and some ethanol blends can conduct electricity; therefore improper grounding and bonding during transloading operations could lead to electrocution hazards and possibly ignition of the fuel.

Ethanol vapor has the potential for formation of explosive mixtures. Uncontrolled impingement of ethanol tank cars after a fire can result in a boiling liquid expanding vapor explosion (BLEVE). Ethanol has a high upper explosive limit and therefore ethanol will burn, or explode even in conditions where oxygen is not readily available, such as within tank cars or in sewers where small airspaces may be present. If released to the soil or groundwater, anaerobic biodegradation of ethanol will produce methane, which can present an explosion hazard if it reaches a confined space.

## **5.2 Potential Exposure Pathways in Spill Situations**

The potential human exposure pathways during spill situations depend on the nature of the spill. In general, given the volatile nature of ethanol and ethanol blends, inhalation exposures are the most likely for both responders and nearby workers or residents. Skin contact (dermal exposure) is possible, but unlikely, since responders would be wearing appropriate protective clothing (see Section 5.5.3). Ingestion exposure is also unlikely, although if the spill reaches surface water, ethanol will dissolve, as discussed in Section 4.3, and could impact a drinking water source. As discussed in Section 3.0 and Appendix A, water supply intakes have been shut down, at least during response actions, during several incidents. In addition, contact could occur as a result of other uses of surface water, such as swimming or boating, or use for cooling or production water. Given the greater likelihood of inhalation exposures during spill situations, this section will focus on health effects related to this route, with limited discussion of other possible routes of exposure.

## **5.3 Human Health Effects**

This section discusses human health effects of ethanol relevant to spill situations. Most of the literature on health effects of ethanol relates to the use or abuse of alcoholic beverages. This information is largely focused on long term exposure by ingestion, and will not be discussed in detail. This section provides information in summary form, and more detail is presented in Appendix C. Table 5-1 provides a summary of effect levels for acute and chronic exposure.

### **5.3.1 Short-Term (Acute) Effects**

Acute ingestion of ethanol can cause headache, nausea, vomiting, drowsiness, fatigue, impaired judgment, lack of coordination, stupor, unconsciousness, and coma. Inhalation can cause eye and upper respiratory tract irritation, fatigue and headache. Dermal contact can result in irritation of skin, with prolonged contact leading to dry skin, cracking, peeling, and itching. Absorption through the skin resulting in other effects is unlikely to be significant.

Ethanol is irritating to eyes and the respiratory system at concentrations of 5,000-10,000 ppm in air. Headaches and other early signs of intoxication were observed in humans when exposed to air concentrations of greater than 3000 ppm for 2 hours, although significant neuromotor effects were not observed in humans exposed to up to 1000 ppm for 6 hours. Similarly, stumbling and lack of coordination were observed in animals after exposure to 4000-10,000 ppm for 8 hrs. Inhalation of 10,000-30,000 ppm for extended periods (8 hrs or more) is lethal to rats. Ingestion of ethanol has caused death in humans, but inhalation of ethanol is unlikely to be lethal.

Rats exposed to E85 at 6130 ppm ethanol and 500 ppm gasoline showed growth effects after 4 weeks of exposure. Recovery was complete by 4 weeks after exposure was stopped. Increased

kidney weight and liver and blood effects were observed primarily with gasoline only exposure. Combined exposure resulted in an additive effect on growth suppression. Inflammation of the upper respiratory tract was observed only with combined exposure.

Data suggest that the threshold for acute alcohol effects following ingestion is in the range of 0.1-0.5 g/kg (corresponding to a blood alcohol level of 0.01%-0.05%). Increased motor activity in rats and increased aggressiveness in monkeys has occurred at these doses. At higher doses, effects on fine motor control and coordination have been observed. Exposure of rats or mice to 20,000 ppm of ethanol in air resulted in significant performance effects, while the lowest dose (12,000 ppm) had borderline effects. To put these exposures in context, rats exposed to 16,000 ppm resulted in an alcohol blood level of 0.05%, a level at which human performance effects are commonly observed.

### 5.3.2 Long-Term (Chronic) Effects

Subchronic and chronic effects associated with alcohol abuse are well documented, and are characterized by progressive liver dysfunction and cirrhosis with chronic ingestion of 2 g/kg/day. Inflammatory and degenerative changes to the heart have also been observed. Neurologic degeneration and effects on the brain structure have been observed after long term high level exposure; however no exposure thresholds for severe effects are available.

**TABLE 5-1 HUMAN HEALTH EFFECTS OF ETHANOL**

<b>ACUTE EFFECTS</b>	
<b>100 ppm in air</b>	Odor threshold
<b>1000 ppm in air</b>	No significant neuromotor effects
<b>3000 ppm in air</b>	Headaches and early signs of intoxication
<b>5000 – 10,000 ppm in air</b>	Irritating to eyes and respiratory system
<b>0.1-0.5 g/kg ingestion (0.01-0.05% blood alcohol)</b>	Threshold for central nervous system effects
<b>CHRONIC EFFECTS</b>	
<b>0.2 g/kg/day ingestion</b>	Threshold for neurological effects in fetuses
<b>2 g/kg/day ingestion</b>	Liver effects
<b>0.5 g/kg/day (50 g/day) Alcoholic beverage and ethanol ingestion</b>	Increased incidence of cancer of the oral cavity, pharynx, esophagus, colorectum, and female breast
<b>20,000 ppm in air</b>	No significant effect on fetuses after exposure of female mice and rabbits during pregnancy

WHO (2010) concluded that alcoholic beverages and ethanol in alcoholic beverages are “carcinogenic to humans”, or Group 1. This category is selected when there is sufficient

evidence of carcinogenicity in humans. They concluded that several types of cancer are caused by alcohol consumption. They also concluded that acetaldehyde, which results from the metabolism of ethanol, contributes to malignant esophageal tumors. WHO (2010) concluded that there is sufficient evidence in experimental animals for the carcinogenicity of both ethanol and acetaldehyde; however, other components of alcoholic beverages may contribute to the observed carcinogenicity. When ethanol was administered in conjunction with other known carcinogens, the carcinogenic effect was enhanced.

Some studies in humans and rodents indicate that ethanol induced genetic effects result from moderate to high levels of ethanol exposure. Rats and mice receiving liquid diets of 5-10% ethanol for 5 or more weeks showed adverse physical and functional effects on testes. Other studies showed that consumption of drinking water containing 15% ethanol or inhalation of 20,000 ppm during pregnancy had no significant effect on fetuses of mice and rabbits.

Fetal alcohol syndrome (FAS) is well known to result from excess alcohol ingestion during pregnancy. More subtle neurological changes in fetuses have also been observed. A threshold for these effects has been identified as 0.5 oz per day (about one drink per day or 0.2 g/kg/day).

### 5.3.3 Health Protective Concentrations

A number of states and regions have developed health-protective concentrations of ethanol in

the environment. These have been developed for various purposes, but none have been promulgated as standards. These concentrations and their bases are summarized in Table 5-2.

TABLE 5-2 HEALTH PROTECTIVE CONCENTRATIONS	
AIR	
53 ppm (100 mg/m <sup>3</sup> )	California Draft Value for protection of public health – based on acute irritancy effects but protective of chronic effects
Chronic – 7.9 ppm (15 mg/m <sup>3</sup> ) Acute – 95 ppm (180 mg/m <sup>3</sup> )	Minnesota Ethanol Sector Specific Interim Exposure Values, for screening purposes at ethanol facilities only – based on irritancy
DRINKING WATER	
1100 mg/L	California Draft Value based on the minimum reporting concentration for ethanol in food (0.5%)
6500 mg/L	NH did not develop drinking water value, but provided value equivalent to drinking 1 beer (13,000 mg ethanol)
0.4 mg/L	NEIWPCC value for comparative purposes, unlikely to increase ethanol in blood over baseline blood concentrations of about 10 mg/L
0.05 mg/L	New York state standard for oxygenates

Table 5-2 shows a wide range of concentrations in drinking water. Both the California and New Hampshire levels are based on exposure by other means that are considered generally acceptable. The California level is based on a concentration in beverages and food of 0.5%, above which ethanol must be reported, and an assumption that 0.5 kg of the daily diet contains this amount. This dose is converted to an equivalent drinking water concentration. Similarly, New Hampshire derived the level shown in Table 5-2 by developing a drinking water concentration equivalent to drinking one beer. Neither of these criteria are based on effects data for ethanol. The New York level is a general level used for oxygenates, and is not specific to ethanol. The NEIWPCC level is based on a drinking water concentration that is unlikely to result in an increased ethanol concentration in blood, and incorporates an uncertainty factor to account for sensitive individuals.

## 5.4 Environmental Effects

A spill of ethanol or ethanol blend could affect soil and vegetation in the immediate area of the spill and fire. In addition, if the spill results in a release to the surface water, aquatic organisms could be affected, as discussed in the following sections.

### 5.4.1 Aquatic Systems

Ethanol released to a water body could directly affect aquatic organisms. Acute toxicity indicates that an effect is observed after a very short period of exposure. Mortality is often measured in the laboratory to various aquatic organisms after short periods of exposure. Such tests typically result in measures of lethal concentrations in water, such as an LC50, a concentration that is lethal to 50% of the test population. In some cases, other effects are studied after acute exposure, such as growth or reproductive effects. Chronic studies involve longer term exposures, and attempt to identify no observable adverse effect levels.

A large number of studies have been conducted on the effects of ethanol on various species, and considering different types of effects. NEIWPCC (2001) evaluated the data available at the time of their report and developed water quality benchmarks for ethanol using EPA Tier II procedures (EPA, 1995). This approach is intended to derive acute and chronic water quality benchmarks for aquatic organisms in cases where data is not sufficient to develop an EPA Water Quality Criteria. They calculated water quality benchmarks using available data for aquatic invertebrates (daphnia species), rainbow trout, and the fathead minnow as shown in Table 5-3.

**TABLE 5-3 WATER QUALITY BENCHMARKS FOR ETHANOL**

<b>Acute</b>	564 mg/L
<b>Chronic</b>	63 mg/L

**Source: NEIWPCC 2001**

In order to determine whether additional aquatic

toxicity information has been generated since the time of the NEIWPCC (2001) evaluation, a search of EPA’s ECOTOX (EPA, 2011) database was conducted for 2001 to the present. Little information was found for the species identified above. Olmstead and LeBlanc (2003) did report that a concentration of 0.5% (5000 mg/L) ethanol had no effect on the production of male progeny in *Daphnia magna* over a chronic exposure period of 21 days. Two additional reports were identified for other species (Chen et al., 2011 and Quinn et al., 2008), but none of these results would change the benchmarks shown above.

Bioconcentration or bioaccumulation of substances in tissues can also be a concern upon releases to water. This is the entry and concentration or accumulation of substances in tissues. The potential for such accumulation is characterized by its octanol/water partition coefficient ( $K_{ow}$ ), which is an indication of a substance’s affinity for fatty tissues. The  $K_{ow}$  for ethanol is 0.49 (HSDB, 2011), indicating that it is unlikely to accumulate in fatty tissues. Such accumulation would also be limited by the expected rapid rate of metabolism.

Oxygen depletion is also a concern with spills to aquatic environments. NEIWPCC (2001) conducted modeling to evaluate potential oxygen depletion effects upon spills to different environments. They used the Streeter-Phelps model to estimate the amount of ethanol required to use up the dissolved oxygen in the stream. This model considers biodegradation and reaeration rates considering small average and large rivers and assuming an initial dissolved oxygen concentration of 7 mg/L. Modeling showed that the oxygen demand needed to biodegrade the benchmark (acute and chronic) levels of ethanol (see Table 5-3) is greater than

<b>TABLE 5-4 ETHANOL CONCENTRATIONS ABLE TO DEplete STREAM DISSOLVED OXYGEN</b>	
<b>Small Stream</b>	56 mg/L
<b>Average River</b>	32 mg/L
<b>Large River</b>	13 mg/L
<b>Source: NEIWPCC 2001</b>	

the amount of oxygen in the stream. Therefore, oxygen depletion in a stream appears to be a more critical impact than direct toxicity of ethanol to aquatic organisms. For comparison purposes, NEIWPCC (2001) calculated ethanol concentrations capable of depleting in stream dissolved oxygen, as shown in Table 5-4. These values are based on the assumption of an initial concentration of dissolved oxygen

concentration of 7 mg/L. However, rivers and streams are considered unimpaired if they have somewhat lower concentrations. For example, in Massachusetts, 314 CMR 4.05 indicates that dissolved oxygen shall not be less than 6 mg/L in cold water fisheries and 5 mg/L in warm water fisheries. If a receiving stream had concentrations lower than 7 mg/L, the concentrations shown in Table 5-4 would be lower.



NEIWPCC (2001) noted that a lower concentration of ethanol is needed in a larger river to deplete the dissolved oxygen because the typical reaeration rate of a larger water body is lower than a smaller water body. They also indicated that if the same volume of ethanol was released to the three environments, the large water bodies would be less impacted than the smaller ones due to increased dilution.

This table indicates that complete oxygen depletion is likely to occur at concentrations lower than those expected to have direct toxicity. In addition, effects on aquatic organisms as a result of low dissolved oxygen will occur prior to complete oxygen depletion. EPA (1986, 2000) has set minimum dissolved oxygen values (over a 24 hour period) at 4 mg/L for freshwater cold water fish and 2.3 mg/L for saltwater aquatic organisms from Cape Cod to Cape Hatteras.



Source: USCG 2000

Oxygen depletion was observed in the case of the Wild Turkey bourbon spill to the Kentucky River, as discussed in Section 3.0. In this case, oxygen in the river was almost completely depleted over about a 6 mile stretch, which migrated downstream, ultimately affecting over 66 miles of the river and resulting in massive fish kills.

## 5.4.2 Terrestrial Systems

Little information is available on the toxicity of ethanol to wildlife. In order to identify any available information, an ECOTOX report (EPA, 2011) was run for terrestrial exposures. Most studies have been done on laboratory or domestic animals, or crops. Many of these studies are intended to provide insight into mechanisms and effects of alcoholism in humans. For example, honey bees have been used as model of human intoxication. In order to provide some insight into the potential toxicity of ethanol to wildlife, some results are summarized in Table 5-5.

In general, exposure to terrestrial organisms is likely to be limited in a spill situation. As discussed in Section 4.5.1, ethanol in surface soil is likely to volatilize, and migrate to deeper soils and groundwater. In addition, it is expected to biodegrade rapidly. Therefore, significant exposure to terrestrial receptors is unlikely to occur. However, localized effects to the soil microbe and invertebrate community may occur in the spill area.

Sample et al., (1996) derived a toxicological benchmark for wildlife based on oral (ingestion) exposure to ethanol. These benchmarks were used to develop concentrations of ethanol in environmental media that would not be hazardous. Due to the lack of availability of wildlife data, their benchmark was based on reproduction effects in rats. They derived a Lowest Observed Adverse Effect Level (LOAEL) of 319 mg/kg/day, and developed a No Observed Adverse Effect Level (NOAEL) of 31.9 mg/kg/day by incorporating a 10 fold safety factor. These values were

adjusted for a variety of wildlife species and then benchmarks developed for food, water, and a combined food and water benchmark for aquatic feeding species. In the absence of empirical data, these values are useful for providing an insight into concentrations in the environment that could result in effects on wildlife, as shown in Table 5-6.

The concentrations in water shown in Table 5-6 are above concentrations that are predicted to result in oxygen depletion (Table 5-4) or result in chronic effects on aquatic organisms (Table 5-3). Therefore, it appears that ethanol in water is a much greater concern for

aquatic organisms than terrestrial organisms. The hazards to wildlife associated with ingestion of food containing ethanol are likely to be low since it is volatile, and does not accumulate in fatty tissue.

**TABLE 5-5 ETHANOL EFFECTS ON WILDLIFE (Select Results)**

<b>Douglas fir Seedlings</b>	Applied ethanol concentrations of 10% and greater lethal within a week, effects also observed with 5% and 1% solutions
<b>Japanese Quail</b>	Ethanol at 2% in drinking water had significant effects on blood, brain weight and growth after 7 day exposure
<b>Honey bees</b>	Bees fed solutions of ethanol (5% and greater) showed behavioral effects, and mortality with solutions of 50% ethanol.
<b>Little brown bat</b>	LD <sub>50</sub> of 3.9-4.4 g/kg

**Source: USEPA 2011 ECOTOX Report**

**TABLE 5-6 ETHANOL WILDLIFE BENCHMARKS (Based on No Observed Effect Levels)**

<b>Food</b>	117 to 471 mg/kg (ppm) depending on species
<b>Water</b>	137 to 521 mg/L (ppm) depending on species
<b>Food and water combined (for aquatic feeding species)</b>	123 to 169 mg/L (ppm) depending on species

**Source: Sample et al. 1996**



## 5.5 Health and Safety Considerations for Responders

### 5.5.1 Recognizing Product Spilled

Section 2.2 shows the DOT placards used for ethanol and ethanol/gasoline blends. These are the best ways of identifying the product spilled. E-95 is generally transported from production facilities to the storage depots by rail. This transport is largely in non-pressurized (general service) tank cars with a capacity of approximately 30,000 gallons (IFCA, 2008). The DOT



Placard for E95 has a red background and a white flame symbol, indicating that it is a flammable liquid. It also shows the North America (NA) code for this substance (1987). Lastly, at the bottom, it shows the hazard class (3). A flammable liquid (Class 3) means a liquid having a flash point of not more than 60.5°C (141°F), or any material in a liquid phase with a flash point at or above 37.8°C (100°F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk packaging.

As shown in Section 2.2, a different placard is used for E10. However, this placard is the same one used for gasoline. This is significant, because E10 requires the use of alcohol resistant foam, as discussed in Section 7.2, while gasoline does not.

### 5.5.2 Exposure Limits

The Occupational Safety and Health Administration (OSHA) has established ethanol Permissible Exposure Limits (PELs) for work place safety (general industry), as shown in Table 5-7. Other occupational values (the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit and the ACGIH Threshold Limit Value) are the same as the

<b>TABLE 5-7 OCCUPATIONAL LIMITS IN AIR</b>		
<b>Limit</b>	<b>Ethanol</b>	<b>Gasoline</b>
<b>OSHA Permissible Exposure Limit (PEL)</b>	<b>1000 ppm (1900 mg/m<sup>3</sup>)</b>	<b>None, 1 ppm for benzene</b>
<b>NIOSH Immediately Dangerous to Life or Health (IDLH)</b>	<b>3300 ppm (6237 mg/m<sup>3</sup>) (10% of the LEL)</b>	<b>None, 500 ppm for benzene</b>

OSHL PEL. PELs are time-weighted average concentrations that must not be exceeded for any 8 hour work shift of a 40 hour week. NIOSH has established a concentration that is deemed to be

Immediately Dangerous to Life or Health (IDLH). In the case of ethanol, this concentration is 10% of the LEL, which is 3.3%. In the case of ethanol, the IDLH is based on the LEL because acute toxicity data do not indicate that the IDLH should be set at a lower value. In comparison, there are no occupational limits for gasoline due to its variable composition. Instead, the PEL and IDLH are shown for benzene, which are substantially lower than those for ethanol.

### 5.5.3 Protective Clothing

Protective clothing to be worn when responding to an ethanol spill, including E85, consists of self-contained breathing apparatus (NRT, 2010). According to NRT (2010), structural firefighters gear will provide limited protection. Contact with skin should be prevented, and Global (2010) recommends the use of nitrile or neoprene gloves for this purpose.

### 5.5.4 Other Health and Safety Considerations

NRT (2010) identifies a number of specific health and safety concerns and recommendations related to spills of fuel grade and E85 ethanol spills. These recommendations are summarized below:

TABLE 5-8 HEALTH AND SAFETY RECOMMENDATIONS FOR SPILLS OF FUEL GRADE ETHANOL AND E85	
EVACUATION	
Large spills	Consider initial downwind evacuation of 300 meters (1000 feet) Consider initial evacuation of 800 meters (1/2 mile) in all directions due to potential for fire spread
Large spills with fire (tank, rail car, or tank truck)	Consider initial evacuation of 800 meters (1/2 mile) in all directions due to potential for fire spread
OTHER CONCERNS	
Electrical conductivity	Good electrical conductor – ground equipment used in handling
Vapors near engine air Intakes	Risk of “runaway engines” if vapors create a rich fuel mixture
Ethanol entering firefighting water intake hoses	Firefighters should avoid drawing raw water with high concentrations of ethanol into intake hoses

## 6.0 *Spill Assessment and Delineation*

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The general spill assessment and delineation process for ethanol and ethanol blend release events is similar to that utilized for petroleum fuel releases. In fact, the characteristics, relative low ecological toxicity and non-visible properties of ethanol dictate that any early assessment and delineation efforts focus primarily upon the more evident and detrimental gasoline components. Nonetheless, there are readily available methods of detection and screening for ethanol which, especially in the event of high concentration blend releases, can be utilized to assess the extent of impact and monitor for ethanol itself. In addition, since the preferred methods are also capable of simultaneously detecting and determining “typical” gasoline components such as BTEX, these methods can effectively delineate and assess the impacts of all components in the event of a release.

### 6.1 *Field Sampling*

As stated previously, the spill assessment and investigation process should mimic that utilized for a petroleum fuel release. This would include screening of ambient air within and outside the release area for the components of interest; visual determination of impacts including stressed vegetation, evidence of impacted aquatic biota, and visual detection of sheens from the gasoline components of blends; statistical determination of appropriate sampling locations and numbers; collection and screening of environmental samples; and the collection and confirmatory analysis of samples. Table 6-1 summarizes the sampling objectives and techniques, which are discussed further below.

The assessment and response phase includes visual observations of impact evidence, screening of ambient air for component detection, and collection of grab samples from impacted matrices for both screening and confirmatory analyses. The list below summarizes the types of observations and/or samples which may be needed to assess the extent and impact of a release. Details on the actual screening tests and analyses are discussed in Sections 6.2 and 6.3, respectively.

**Visual Observations** - look for evidence of sheen from gasoline components, evidence of biota impacts (dead fish, stressed vegetation, etc.). Ethanol is colorless and water-soluble and cannot be seen in water. Wet spots on soils or solid surfaces should be investigated and screened for properties such as flammability to determine if they are spilled product. Pooled liquids and even surface waters can be quickly screened for flammability and/or ethanol content, as a percentage; see Section 6.2 for details.

**Ambient Air Screening** – flammability (LEL) can be used as an indicator of presence/absence of ethanol and ethanol blends. Real-time screening of air can be conducted for presence of vapor-phase concentrations of ethanol and ethanol blend components, and, longer term (8-hour) exposure monitoring can be conducted within and outside spill zone (NIOSH methods).

**Collection of Samples from Environmental Media** - grab samples can be collected of site soils, sediments, surface waters, and groundwater, depending upon the extent of release and exposed media. Since ethanol is rapidly biodegraded, water samples intended for off-site shipment must be preserved at a pH<2. Soil and sediment samples for confirmatory analysis must be collected using acceptable VOC sampling and preservation methods.

**TABLE 6-1 SAMPLING TECHNIQUES**

Objective	Matrix	Techniques
Determine immediate extent of spill and impact-including during first responder efforts	Surface water, surface soil, paved surfaces	<ul style="list-style-type: none"> <li>Visual observation-sheens from denaturing additives (gasoline), visible fires, pooled large volumes of liquid</li> <li>Stressed vegetation, dead fish or animals</li> <li>Quick flammability screen</li> <li>Hydrometer-water samples only</li> </ul>
Determine extent and hazard of ambient air in spill area and immediate vicinity	Air- Real-Time Monitoring	<ul style="list-style-type: none"> <li>LEL-flammability</li> <li>Indicating tube-target ethanol or benzene</li> <li>PID-targets gasoline components (BTEX)</li> <li>FT-IR- can differentiate ethanol and gasoline components (BTEX)</li> </ul>
Determine vertical and horizontal extent of environmental impacts in site surface water, soils, and groundwater	Ground and surface water, soil	<ul style="list-style-type: none"> <li>Grab samples for either on-site screening or laboratory analysis.</li> <li>Water samples to be analyzed for ethanol must be collected and preserved as for VOCs</li> <li>Soil samples must be collected using closed-loop sampling methods</li> </ul>
Determine potential off-site impacts to nearby air-receptors	Air	<ul style="list-style-type: none"> <li>8-hour samples using absorption tube methods (NIOSH 1400)</li> </ul>

## 6.2 Screening Methods

Although there are a multitude of rapid screening methods for the gasoline components in ethanol fuel blends, the properties of ethanol make development of rapid detection methods more of a challenge. Ethanol's ionization potential (10.47ev) is close to that of a typical lamp (10.6ev) found in Photoionization Detectors (PID), resulting in it being a low-response compound to PID screening instruments (isobutylene Correction Factor (CF) of 10 using a 10.6ev lamp and 3.1 using a 11.7ev lamp). Although it can be easily detected via Flame Ionization Detectors (FID), the non-specificity of this detector makes it difficult to differentiate ethanol without chromatographic separation. There is no readily available spot test or immunoassay screen for ethanol. In addition, its water solubility makes it a poor candidate for the typical field-portable GC instruments which measure headspace or use purge and trap introduction and cannot tolerate

direct aqueous injections. The available screening methods for ethanol are summarized in Table 6-2, and discussed below:

TABLE 6-2 ETHANOL SPILL SCREENING TECHNIQUES			
Method	Technique/Detector	Detection Limit	Comments
Quick Screens for Presence/Absence			
Open flame test	Exposing small volume of material to open flame	Presence/Absence	<ul style="list-style-type: none"> <li>Identifies relatively high concentration of ethanol and/or gasoline (still flammable)</li> </ul>
Percent Ethanol Check-water only	Hydrometer	1-percent	<ul style="list-style-type: none"> <li>Results will be biased low if gasoline mixture</li> </ul>
Air			
Real time monitoring for flammability	LEL monitor-calibrated versus methane	1-percent of LEL	<ul style="list-style-type: none"> <li>Correction Factor (CF)=1.5</li> </ul>
Color Tube	Air pumped through reactive sorbent-color change occurs based upon concentration	Ethanol-1000 ppm Benzene-5-40 ppm	<ul style="list-style-type: none"> <li>Need separate tubes for each analyte</li> <li>Ethanol tube requires the volume of a 1-hr sample to achieve limits</li> <li>One-time use</li> </ul>
Real-time monitoring w/PID	Air pumped into chamber with a photo-ionization detector-calibrated versus isobutylene	Ethanol-50-100 ppm Benzene- 5-20 ppm	<ul style="list-style-type: none"> <li>Non-selective</li> <li>C F =10 for 10.6ev lamp</li> <li>CF = 3.1 for 11.7ev lamp</li> <li>Response to gasoline components (BTEX) greater than ethanol</li> </ul>
Real-time monitoring w/FID	Air pumped through chamber, detected via flame ionization	Ethanol-50-100 ppm Benzene- 5-20 ppm	<ul style="list-style-type: none"> <li>Non-selective</li> </ul>
Real-time monitoring w/FT-IR	Air pumped into chamber where it is subjected to excitation and the resulting infra-red spectral bands are detected. FT-IR peaks are unique to particular compounds	Ethanol-25 ppm Benzene- 200 ppb	<ul style="list-style-type: none"> <li>Selective and can screen simultaneously since bands for ethanol (<math>3500\text{ cm}^{-1}</math>) and BTEX (<math>2500\text{-}2000\text{ cm}^{-1}</math>) are separated</li> <li>Ethanol and BTEX in compound library</li> </ul>
Water			
Screen for impact in surface water bodies	Dissolved oxygen probe biochemical oxygen demand, chemical oxygen demand per standard methods	0.5 mg/l dissolved oxygen	<ul style="list-style-type: none"> <li>Can be used to identify impact to surface water and monitor recovery</li> </ul>
Headspace with GC using detection by FID, PID, or MS	Measured volume of sample with known headspace is allowed to equilibrate and a volume of the headspace injected for comparison to similarly prepared standards	Ethanol-5-100 mg/l Benzene- 5-50 ug/l	<ul style="list-style-type: none"> <li>Ethanol is water-soluble, will not enter the headspace well-resulting in the high limit of detection</li> <li>Ethanol is a poor responder to the PID</li> </ul>
Direct injection onto a GC with detection via FID, PID, or MS	Known volume injected onto the GC and the compounds separated and detected. Comparison to standards	Ethanol-5 mg/l Benzene-250 ug/l	<ul style="list-style-type: none"> <li>Ethanol is a poor responder to the PID</li> </ul>
Portable GC with Purge & Trap system-detection via PID, FID, or MS	Known volume sparged through a sorbent media which is then backflushed under rapid heating to force trapped compounds into the GC. Comparison to standards	Ethanol-200 ug/l Benzene- 5 ug/l	<ul style="list-style-type: none"> <li>Ethanol is water-soluble, and exhibits low purge efficiency resulting in the high limit of detection</li> <li>Ethanol responds poorly to PID</li> </ul>

TABLE 6-2 ETHANOL SPILL SCREENING TECHNIQUES (continued)

Method	Technique/Detector	Detection Limit	Comments
Soils and Sediments			
Headspace with GC using detection by FID, PID, or MS	Measured mass of sample is added to a known volume of water with known headspace and allowed to equilibrate; headspace injected onto the system for comparison to similarly prepared standards	Ethanol-100 mg/kg Benzene- 50-500 ug/kg	<ul style="list-style-type: none"> <li>Ethanol is water-soluble, will not enter the headspace well- resulting in the high limit of detection</li> <li>Ethanol is a poor responder to the PID</li> </ul>
Direct injection onto a GC with detection via FID, PID, or MS	Measured mass of sample is added to a known volume of water; injected onto the GC and compounds separated and detected. Comparison to standards	Ethanol-1-5 mg/kg Benzene-250 ug/kg	None
Portable GC with Purge & Trap system-detection via PID,FID, or MS	Measured mass of sample added to known volume of solvent and then a known volume is placed into a vessel containing water. The sample/solvent/water volume is sparged through a sorbent media which is then backflushed under rapid heating to force trapped compounds into the GC. Comparison to standards	Ethanol-500 ug/kg Benzene- 50 ug/kg	<ul style="list-style-type: none"> <li>Ethanol is water-soluble, and exhibits low purge efficiency resulting in the high limit of detection</li> <li>Ethanol responds poorly to PID</li> </ul>

## Screening Presence/Absence-Soils and Waters

One of the simplest ways to ascertain whether or not ethanol and/or blends are present in media is via a simple open-flame burn test. This can yield valuable information, especially when performing the visual observation/delineation phase of spill site assessment. There are two basic means to perform a quick flame test.

- Place a very small volume or mass of the material into a shallow container such as a watch glass or even a small pie tin and wave a lighted match or a propane torch above the sample; or
- Make a small loop in a length of copper wire, dip it into the sample, and then place it into an open flame.

In either case, if the sample (or wire) burns, sparks, or otherwise supports combustion the spilled product is present in the test sample.

## Gross Screening-Water using a Hydrometer

A quick estimate (percentage) screen for ethanol can be performed via a simple hydrometer test, like those used in ethanol plants and distilleries. A sample of sufficient size is placed into a container and the hydrometer floated into it. The percent ethanol can be read as the point on the

hydrometer scale that intersects the liquid meniscus. The reading will be biased low if gasoline is present. Although the hydrometer is calibrated at 60°F, the actual correction to the reading varies by less than 1% as temperature falls to 0°F and 6% (adjust higher) at an ambient temperature of 120°F. Therefore, for purposes of screening for gross concentration the method is viable without correction. A field SOP, based upon the ASTM Method (1250) is provided in Appendix D.

### **Ambient Air Field Screening**

Color-indicating tubes are available for ethanol. These will provide rapid single analysis for the compound. However, the air volume required to meet the stated detection limits requires a 1-hour collection time at standard input flows, making use of a color indicating tube a poor choice for real-time data needs. Ethanol is a poor responder to a PID. It does respond to a portable FID, this detector also responds to other volatile organic compounds, including methane. If real-time and simultaneous detection of ethanol and gasoline components is necessary, the best available technology is a portable Fourier Transform Infrared (FT-IR) spectrometer, available from several manufacturers. These instruments are capable of low ppm detection in air, contain pre-loaded compound libraries which include ethanol, and can simultaneously screen for up to 25 compounds including the major components of gasoline. Detection and quantitation of ethanol is accomplished by using the response at the wavelength corresponding to the O-H stretch at approximately  $3500\text{ cm}^{-1}$ . The BTEX components are evaluated via the aromatic ring wavelengths at  $2500\text{--}2000\text{ cm}^{-1}$ . Thus, the method can provide absolute selectivity and separate screening data even in low ethanol blend events.

### **Soil/Sediment and Water Field Screening**

Environmental matrix samples can be field-screened using typically available portable gas chromatographs (GCs). Detection via FID or mass spectrometry (MS) is preferred as ethanol is a poor responder to a PID. Detection limits will be elevated in most of these systems due to ethanol's solubility in water and its poor purge efficiency. This is because most field portable GC systems use headspace or purge and trap sample introduction methods and are not designed for direct liquid injection onto the GC column. Although gasoline components volatilize easily into sample headspace and are also readily purgeable, ethanol is water soluble, less likely to quickly enter sample headspace and difficult to purge. These properties result in elevated detection limits (see Table 6-2) for ethanol compared to benzene, for example. However, even this elevated detection limit data can be useful in assessing impacts. If a field portable GC system capable of accepting direct liquid injections is available, detection limits will be similar to those reached in fixed-based laboratories utilizing published methods, as shown in Table 6-3.



As an alternative to field or laboratory measurements of ethanol, measurements of dissolved oxygen and biochemical oxygen demand can be used, especially in surface water, to monitor the impact of ethanol releases over distance and time.

### 6.3 *Analytical Methods*

There are several published and well known procedures for analysis of the gasoline components of ethanol blends. Since ethanol is an industrial chemical and requires monitoring in the work place, both NIOSH and OSHA published methods for its determination several years ago. However, while ethanol has been determined in biological matrices for toxicology and criminology for many years, it was only recently considered as a target in environmental matrices. Environmental laboratories have determined ethanol primarily by modifying existing methods; such as SW-8015 or by adding it to mass-spectrometry libraries and target compound lists used for routine VOC analysis, but the analyte was never listed by EPA as a potential target analyte within the methods themselves. Recently, EPA developed methods that can more efficiently extract water-soluble polar organics from environmental matrices and improve efficiency and detection-limits using GC or GC/MS techniques. Manufacturers are just now producing commercially available instruments that perform these methods. Available methods are summarized in Table 6-3, and discussed below.

**Air** - Both the NIOSH (1400) and OSHA (100) methods rely on collection onto an adsorption tube, extraction via desorption solvent, and GC-FID quantitation. NIOSH 1400 uses an activated charcoal collection tube and a dimethyl formamide/carbon disulfide extraction system. The OSHA method (100) uses an Anosorb™ collection tube and desorption. Commercial laboratories which perform both analyses are readily available.

Although, air samples may also be collected and analyzed using SUMMA canisters, like other polar and water-soluble analytes, ethanol tends to “stick” to the canister and valve surfaces under typical analysis conditions resulting in poor efficiency and elevated detection limits.

**Water, Soils, and Sediments** - the most prevalent methods for determining ethanol in environmental matrices utilize direct-injection techniques and GC-FID using wide-bore capillary columns coated with highly polar stationary phases designed for separation of alcohols. Laboratories usually refer to these methods as 8015M when citing procedures. Direct injection methods yield detection-limits in the low ppm range for both waters and soils/sediments.

Laboratories may also analyze samples for ethanol by GC/MS using the purge and trap techniques (methods 5030A and 5035A). Due to ethanol’s solubility in water and low purge-efficiency, detection-limits are in the 100-250 ppb range for waters and soils/sediments.



**TABLE 6-3 ANALYTICAL METHODS**

Method	Technique/Detector	Detection Limit	Comments
<b>Air</b>			
NIOSH 1400	Air pumped through charcoal sorbent tube. Tube is desorbed using solvent system and the compounds in solution determined by GC-FID	Ethanol-20 ppm Benzene-5 ppm	None
OSHA 100	Air is pumped through a Anosorb™ 747 sorbent tube. Tube is desorbed using a solvent system and the compounds in solution determined by GC-FID	Ethanol-100 ppm Benzene- 5 ppm	None
<b>Water</b>			
SW-846 Modified Method 8015M	Direct injection onto a GC-FID system	Ethanol-25 mg/l Benzene- 500 ug/l	None
SW-846 5030 with quantitation via 8015M or 8260 8021 for BTEX	Purge and trap with GC-FID or GC-MS detection GC-PID for BTEX	Ethanol-500 ug/l Benzene-0.5 ug/l	Ethanol is water soluble and has low purge efficiency
SW-846 5031	Azeotropic distillation with quantitation of the resulting solution via 8015M or 8260	Ethanol-10 ug/l	No commercially available instrument. Expensive and difficult to find a lab performing
SW-846 8261	Vacuum distillation (SW-5032) with quantitation via GC-MS	Ethanol-10 ug/l	Instrumentation available but only major lab networks offer analysis
<b>Soils and Sediments</b>			
SW-846 Modified Method 8015M Method 8021	Measured mass dilution in water, direct injection onto a GC-FID system GC-PID for BTEX	Ethanol-500 ug/kg Benzene- 100 ug/kg	None
SW-846 5035 with quantitation via 8015M or 8260	Closed-loop purge and trap with GC-FID or GC-MS detection	Ethanol-50 ug/kg Benzene-0.5 ug/kg	Ethanol is water soluble and has low purge efficiency
SW-846 5031	Azeotropic distillation with quantitation of the resulting solution via 8015M or 8260	Ethanol-5 ug/kg	No commercially available instrument. Expensive and difficult to find a lab performing
SW-846 8261	Vacuum distillation (SW-5032) with quantitation via GC-MS	Ethanol-5 ug/kg	Instrumentation available but only major lab networks offer analysis

**Newer EPA Methods** - during the 1990's EPA began looking at ways to improve detection limits for polar organics such as ethanol. There were two alternative extraction methods published in SW-846. Method 5031 utilizes azeotropic distillation methods and allows for



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analysis of the extracted analytes by GC or GC/MS. Method 5032 uses vacuum distillation and was also developed for use with either GC or GC/MS quantitation methods. Both methods were developed by the EPA laboratories and required substantial equipment set-up and in some cases construction of the required apparatus. These methods were, therefore, slow to be recognized by the environmental analysis community and manufacturers. To date no commercial company has produced an instrument for performing Method 5031. Recently, instruments became available to perform vacuum distillation. EPA in 2007 published Method 8261 which is a vacuum distillation GC/MS procedure. Ethanol is specifically listed as a potential target analyte in this method (see Table 6-3).

## **7.0 Response Options**

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### **7.1 General Description**

Although ethanol and ethanol blend spills are similar to other fuel release scenarios, the physical and chemical properties of ethanol add unique challenges and alter remediation approaches. Ethanol, unlike gasoline, is water soluble and even in blends will enter solution if exposed to water. This means that in ethanol blend spills there is a potential for a layered spill profile, gasoline floating on the water surface and ethanol mixing into the water) requiring two different clean-up strategies. The following sections describe short term and longer term response priorities. These sections are followed by media-specific options.

#### **7.1.1 Short Term Response Priorities**

The priorities of first responders are life safety, incident stabilization, and property conservation. It is not the objective of this report to provide guidance as to how to conduct these activities in the event of an ethanol spill. Rather, it is to provide guidance as to the potential for long term impacts of various options.

First responders must utilize techniques and products that will counter both the water-solubility and flammability of ethanol. In many cases, fires result during spill events, and containment of such fires is often an effective response strategy (contained burn). As discussed in Section 3.0 and Appendix A, burning in many large spill situations has greatly reduced the mass of ethanol that reached environmental media. The products of ethanol combustion are carbon dioxide and water. Under ideal conditions of wind direction and speed, ground cover, proximity to structures, and other site-specific elements, the best approach may be to conduct a controlled burn.

While water can be used to cool structures and misting can be used to keep vapors down, the application of water to an ethanol fire, unless in sufficient volume, does not substantially decrease the flammability of ethanol. The use of water also results in an increased potential for migration of ethanol solution to storm and sanitary sewer lines, groundwater, and surface water, unless it is recovered.

Fire-fighting foams can be effective, but must be alcohol resistant (AR-FFF), or rapid degradation and loss of the foam blanket can occur. Unless recovery of the foam/ethanol occurs, the potential for migration to storm and sanitary sewer lines, groundwater and surface water is still present. The foam and ethanol mixture will result in increased

biochemical oxygen demand /chemical oxygen demand loading to wastewater treatment facilities or surface water compared to the ethanol alone.

Any efforts by first responders to control or prevent migration of ethanol will have benefits in reducing future response actions to address groundwater or surface water impacts. Recovery of ethanol from soil or other surfaces will eliminate a flammability hazard, and reduce impacts to groundwater and surface water. Physical barriers, such as booms or plastic-lined earthen dams, can be effective in preventing flow of ethanol to larger surface water bodies. Booms for such purposes must be designed to absorb water-soluble materials. Physical barriers are only effective in blocking progress into water bodies or ditches and afford little control once the ethanol has entered a water body.

### **7.1.2 Longer Term Response Priorities**

Longer term response priorities are focused on preventing migration of ethanol from the spill site. This can include removal of spilled material, soil removal, damming of creeks or ditches, aeration, etc. These activities are designed to prevent migration of ethanol to both groundwater and surface water, as well as eliminating possible flammability and explosion hazards, as discussed in the following sections.

## **7.2 Media Specific Options**

### **7.2.1 Soil**

Ethanol spills on surface soils present unique challenges to first responders and follow-up remediation teams. Except under cold winter conditions, ethanol spills pose a significant flammability hazard. The water solubility of ethanol allows it to rapidly migrate into and through soils, especially those with higher moisture content. Thus, any response strategy must be able to quickly eliminate the flammability hazard and suppress the potential movement of the spill both laterally and through the soil column. Response options for such spills are summarized in Table 7-1, as well as the conditions required for implementation and possible issues.

### **Contained/Controlled Burn**

Under ideal conditions of wind direction and speed, ground cover, distance from structures, and other site-specific elements, the best approach to eliminating the flammability hazard and minimizing movement of ethanol through soil may be to allow the product to burn and/or conduct a controlled burn of the spilled product. Unlike methanol, ethanol does burn with a visible flame, especially when denatured with low percentages of gasoline. Contained/controlled burns must be conducted with the oversight, guidance and approval of the local fire officials and appropriate precautions

must be taken to protect areas outside the burn zone and conduct sufficient monitoring to both protect and satisfy the public. Monitoring should include both chemical and physical elements; such as particulate matter in smoke.

This method actually leaves little waste and there is no need to dispose of any residuals; all of the ethanol and/or ethanol blend is thermally destroyed. The risk associated with this method include unexpected changes in wind direction and/or speed causing the burn profile to shift, public exposure to the smoke and byproducts, and the overall perception of an outdoor burn of a chemical spill.

As described in Section 3.0, this method has been used effectively in several ethanol incidents that have occurred, including the New Brighton, PA and Arcadia, Ohio spills. However, in both cases, releases to surface water also occurred. In the case of New Brighton, PA, tank cars entered the river resulting in a direct release of ethanol to surface water. In the case of Arcadia, OH, however, some of the ethanol released to the surface did not immediately burn. Evidently pooled product permeated the snow and ice blanket, entered the underlying soil, and migrated to the field drainage systems resulting in impacts to the drainage water.

### **Foam Suppression with Water Flush**

In situations where the spill has occurred in close proximity to storm water inlets or catch basins, the most effective response may be to combine vapor suppression with copious flushing. Alcohol resistant foam (AR-FFF) must be used or the ethanol will literally react with and break down the vapor barrier. Although AR-FFF products are biodegradable, they can have effects on the environment in the short-term (through direct toxicity or oxygen depletion) and both they and the ethanol itself can be toxic to water treatment bio-remediation systems in high concentration. In addition, vapor suppression foams only suppress the ethanol vapor and do not significantly affect concentration. Dilution in the range of 5-10X with water is necessary to produce foam and ethanol concentrations that will not affect publicly owned treatment works (POTW) bio-digestion systems.

Because of the significant volumes of water that the method requires, this process is best for smaller spills and in soils near POTW intakes. It is also better suited to surfaces such as gravel, hard-pan soils and clays that will not produce large volumes of wet mud when flushed with water. Obviously, it is a poor choice in areas near surface water bodies that could be negatively impacted by the run-off from the flushing process.

**TABLE 7-1 RESPONSE OPTIONS FOR SURFACE SOIL SPILLS**

Method	Conditions Required	Issues with Approach
Controlled/contained burn of pooled liquids	<ul style="list-style-type: none"> <li>Wind speed and direction away from structures</li> <li>Open area not near structures or other flammable materials</li> </ul>	<ul style="list-style-type: none"> <li>Local authorities responsible for public safety</li> <li>Sudden wind shift could threaten other structures/areas</li> </ul>
Foam suppression and water flush	<ul style="list-style-type: none"> <li>Near sewer or storm drains that go to POTW</li> <li>Ability to recover foam/ethanol</li> <li>Works best if soils are hard and won't produce too much mud</li> <li>Should not be used near surface water bodies, unless access can be blocked</li> </ul>	<ul style="list-style-type: none"> <li>Foam and ethanol/fuel blends require dilution to keep from affecting POTW</li> <li>Foam in surface water can cause oxygen depletion, and can be toxic to aquatic species</li> <li>Ethanol can still affect groundwater unless recovered</li> <li>Ethanol/foam mixture can still affect surface water (biochemical oxygen demand)</li> </ul>
Pooled Liquid Removal, Soil Excavation and Off-site Disposal	<ul style="list-style-type: none"> <li>Temperatures that limit flammability, ability to wet mist work zone</li> <li>Viable landfill or treatment/disposal facility</li> <li>Cost-effective soil volume impact zone</li> </ul>	<ul style="list-style-type: none"> <li>Must monitor and control work zone for flammability</li> <li>If using vacuum methods to remove foam/water/ethanol mixtures may need to add dispersant to prevent re-expansion of foam</li> <li>Excavated soils must be screened for flammability</li> <li>Flammable (FP&lt;140F) soils cannot be transported and must be wetted or otherwise rendered non-flammable</li> </ul>
In-place Mixing and Evaporation	<ul style="list-style-type: none"> <li>Temperatures that limit flammability</li> <li>Ability to wet mist work zone</li> </ul>	<ul style="list-style-type: none"> <li>Must monitor and control work zone for flammability</li> <li>Large impact areas should be divided into working grids</li> </ul>

### Removal and Off-site Disposal

In spills where the product covers large areas of soil and is slow to evaporate, it may be necessary to physically remove the pooled liquids and impacted soils. Pooled liquids and even high concentrations in soils can produce enough vapors to become a fire hazard. They may also impact groundwater and/or surface water. In addition, fire-fighting foam residuals can have effects on the environment and unless broken down with available dispersants may re-expand and cause difficulties, especially if a vac truck or Vactor is used to remove them.

Appropriate safety precautions must be observed. These include continual monitoring of potential flammability of the work zone and isolation of non-involved personnel. A fine water mist can be used to both wet/dilute the ethanol and keep vapors down while the operation is in process. Residual liquids including ethanol/water/foam mixtures can be removed via vac truck or Vactor if the flammability conditions allow. If large amounts of foam are present it may be necessary to add dispersants to the mix to prevent re-expansion during removal. Excavated soils should be screened for flammability, (flash point tested) for safety and transport purposes. If a non-intrusive excavation method is used such as a Vactor hydro/air excavator, extreme caution must be observed if free

potentially flammable liquids are present. Disposal options include landfill, bio-treatment, or low-temperature thermal treatment. However, none of these options is applicable to soils which are flammable (FP<140°F). Therefore, any soils which have this potential issue must have their flammability lowered either through natural evaporation or wetting of the matrix.

### **In-Place Mixing/Evaporation**

For very large impact areas where controlled burning is not possible and off-site disposal is not feasible, the only option may be to physically mix and manipulate the soils, thus enhancing the natural volatilization of the ethanol. The objective of this approach is to safely encourage sufficient volatilization to reduce the concentrations to the point where the matrix is no longer toxic and natural bio-degradation is supported. Vapor suppression methods such as water misting should be employed and the work zone must be controlled and monitored for flammability. In large spills, the work area can be divided into working grids and each grid screened for residual ethanol through flammability testing; such as a simple open flame burn test. Soils containing insufficient ethanol to burn will rapidly biodegrade if left to do so.

### **7.2.2 Groundwater**

If a release of a high ethanol content material impacts the groundwater, the same properties of ethanol that limit clean-up in surface water bodies apply. Response options for groundwater impacted by an ethanol or ethanol blend spill are summarized in Table 7-2. Ethanol will rapidly dissolve and disperse into groundwater. It may also increase the mobility of any gasoline components present in the blend. Being water soluble and mobile, there are few immediate response options available. However, bio-degradation will commence quickly as the plume concentration is reduced. In zones of higher concentrations, groundwater treatment options are limited to sparging and pump and treat methods using carbon. These methods have limited efficiency due to the high solubility of ethanol, but they can be used to reduce high concentrations to more treatable levels by

**TABLE 7-2 RESPONSE OPTIONS FOR SPILLS IMPACTING GROUNDWATER**

Method	Issues with Approach
<b>Water treatment with sand/GAC</b>	<ul style="list-style-type: none"> <li>Carbon has limited effectiveness on ethanol</li> <li>Will address gasoline components</li> </ul>
<b>Air sparging</b>	<ul style="list-style-type: none"> <li>Ethanol has limited sparge efficiency</li> <li>Works well on gasoline components</li> </ul>
<b>Bio-augmentation Bio-venting</b>	<ul style="list-style-type: none"> <li>Both ethanol and gasoline components respond well</li> <li>Will not work in high ethanol concentration systems</li> </ul>
<b>Monitored Natural Attenuation</b>	<ul style="list-style-type: none"> <li>Ethanol is highly and naturally biodegradable</li> </ul>



other means. *In situ* methods other than bio-augmentation are not applicable and the bio-degradation process is inhibited at high concentration levels.

### 7.2.3 Surface water

Spills in surface water bodies leave few options. Table 7-3 summarizes the available options, and possible issues. Ethanol is water-soluble and will quickly migrate through

TABLE 7-3 RESPONSE OPTIONS FOR SURFACE WATER SPILLS

Surface Water Type	Approaches	Issues
Ditches, Small Creeks, Streams, and Rivers	<ul style="list-style-type: none"> <li>• Earthen dams to block outlets to other waters</li> <li>• Remove/dispose of ethanol/water mixture</li> <li>• If dissolved oxygen levels impacted and biota affected, aerate to replace dissolved oxygen</li> </ul>	<ul style="list-style-type: none"> <li>• Ethanol is water soluble and will not be stopped by typical boom or hay bales.</li> <li>• Removal effective in ditches and small pools</li> <li>• Water treatment using typical sand/carbon filter portable systems will have limited effect on ethanol levels, but will reduce BTEX</li> </ul>
Large Rivers, Ponds and Lakes	<ul style="list-style-type: none"> <li>• Deploy boom or construct earthen dam(s) to prevent further infiltration/discharge</li> <li>• Gasoline components can be removed by surface boom</li> <li>• Aeration can be used to improve/prevent depleted dissolved oxygen</li> </ul>	<ul style="list-style-type: none"> <li>• Limited response options available</li> <li>• Notify downstream water intake plants so they may take necessary actions</li> <li>• Water treatment using typical sand/carbon filter portable systems will have limited effect on ethanol levels, but will reduce BTEX</li> <li>• Deployment of aeration equipment for large rivers, lakes and ponds may take time</li> <li>• Pond aerators can be used for smaller ponds</li> </ul>
Freshwater Wetlands	<ul style="list-style-type: none"> <li>• Deploy boom or construct earthen dam(s) to prevent further infiltration/discharge</li> <li>• Gasoline components can be removed by surface boom.</li> <li>• During low-water conditions remove pooled liquids and/or use controlled burn methods to prevent migration</li> <li>• Aeration can be used to improve/prevent depleted dissolved oxygen</li> </ul>	<ul style="list-style-type: none"> <li>• Limited response options available, especially during high water conditions</li> <li>• Water treatment using typical sand/carbon filter portable systems will have limited effect on ethanol levels, but will reduce BTEX</li> </ul>
Saltwater/Tidal Wetlands	<ul style="list-style-type: none"> <li>• Deploy boom or construct earthen dam(s) to prevent further infiltration</li> <li>• Gasoline components can be removed by surface boom.</li> <li>• During low-water conditions remove pooled liquids and/or use controlled burn methods to prevent reentry into marine habitat</li> <li>• Aeration can be used to improve depleted dissolved oxygen</li> </ul>	<ul style="list-style-type: none"> <li>• Limited response options available - Important to perform as much removal/elimination as possible during low water/tidal conditions.</li> <li>• Water treatment using typical sand/carbon filter portable systems will have limited effect on ethanol levels, but will reduce BTEX</li> </ul>
Marine-inner harbor	<ul style="list-style-type: none"> <li>• Gasoline components can be managed by surface boom.</li> <li>• Mixing and aeration can be used to improve dispersion and dissolved oxygen</li> </ul>	<ul style="list-style-type: none"> <li>• Limited response options available and mostly target BTEX components of gasoline</li> </ul>
Marine-outer harbor	<ul style="list-style-type: none"> <li>• Deeper water and varied currents make dissolved oxygen replacement difficult</li> </ul>	<ul style="list-style-type: none"> <li>• Very limited options focused entirely on non-ethanol components</li> </ul>
Open ocean	<ul style="list-style-type: none"> <li>• No viable means of removing or counteracting ethanol effects</li> </ul>	<ul style="list-style-type: none"> <li>• Response focuses on gasoline components</li> <li>• Ethanol allowed to run its course</li> </ul>



the matrix. Being water soluble and quickly biodegraded, reduction in dissolved oxygen can result in fish kills. Such effects will continue until sufficient dilution has occurred to reduce toxicity. Response options depend upon the types of surface water structures impacted and are discussed in the next several sub-sections.

### Ditches

If the spill is confined to a ditch with slow-moving water, the best response is to dam the ditch down-stream of the site or just up-stream of any threatened water body. Earthen



Impacts to Stream  
Painesville, Ohio  
Source: Ohio EPA 2007

dams can be effective in preventing migration to surface water. In cases where flow cannot be prevented, rip-rap can be used in the construction of earthen dams to increase turbulence and aeration. Typical emergency response dams such as those made of hay bales will not stop movement of the ethanol since it is water-soluble. Booming is ineffective for the same reason.

Once the impact zone is confined and defined, the ethanol can be left to naturally evaporate and degrade. If faster removal is required, options include sparging (via aeration) or

active water treatment with discharge.

Pond aerators can be placed within the ditch to perform the sparging. Active water treatment consisting of typical skid-mounted sand/carbon systems will remove both the ethanol and gasoline components, although removal of ethanol will be limited.

Below is shown a simple aeration system implemented at the Bryan Ohio spill. The liner



Aeration of Stream, Bryan,  
Ohio  
Source: Ohio EPA

is used to prevent infiltration to groundwater. Aeration is used over short stretch of the stream to increase oxygen content.

### Small Streams and Rivers

If spills occur into moving water systems ethanol's solubility will limit response options. The only recourse is to get downstream of the spill and block its

progress or to simply allow it to run its course until dilution eliminates impacts. Aeration can be used to reduce or restore oxygen depletion. Any blocks/dams must be constructed to block or significantly impede water or dissolved ethanol will not be controlled.

### Large Rivers

Aside from keeping spills from entering larger rivers by blocking progress through smaller streams and tributaries, there is little that can be done if material enters or is released into a large river. Any downstream municipal plants must be notified of the spill so that they may shut-off intakes and avoid reduction of loss of biological activity in their wastewater treatment processes. Down flow industrial facilities which are using the source for process water should also be notified in case ethanol could react negatively with their process. In extreme cases, treat and release systems may be required upstream of water plants to protect them from harmful concentrations of ethanol. In some cases, aeration may be used to prevent or improve anoxic conditions resulting from the biodegradation of ethanol. This was used in the case of the Wild Turkey Distillery release to the Kentucky River, although only after a significant fish kill occurred. It may be difficult to use such techniques to prevent such effects due to difficulties with the deployment of such equipment in a sufficiently timely way.



### Ponds and Lakes

When spills occur into ponds and lakes, response options for the ethanol component are limited at best. Since ethanol is water soluble it will rapidly disperse into the water body

and follow any underwater currents. If the spill occurs into a smaller body such as a farm or residential pond, techniques such as aeration can be deployed to reduce concentrations and oxygen depletion. Active pump and treat systems can also be employed. In larger water bodies these methods would have limited influence and aside from preventing additional release from the spill source there is little that can be done aside from allowing the ethanol to dilute to a non-toxic level so that natural degradation can begin. As discussed above, aeration techniques can be used, but the timeliness of such techniques is critical.

#### **7.2.4 Wetlands**

Spills occurring in wetland environments pose unique challenges. Response options will depend upon factors such as size and depth of the wetland/marsh, proximity to larger open water, and in the case of tidal marshes, the tide stage and resulting water levels. Ethanol impacts fresh and salt water in the same way and will rapidly dissolve into both, as well as into brackish waters in estuaries and tidal rivers. Thus, options are once again constrained by the rapid dispersion of ethanol and its solubility in the water.

##### **Freshwater Marsh/Wetland**

Response to spills in freshwater marsh/wetland areas depends upon factors such as the size and depth of the impacted area. Spills in small shallow marshes are most likely to result in high toxicity conditions as the dilution effects are greatly reduced. In these cases, aeration, using typical pond aerators can help reduce ethanol concentrations and avoid oxygen depletion. Although ethanol is soluble in water and actually forms an azeotrope, it can be sparged from the water. The low efficiency will allow for aeration to be utilized without fear of creating a flammable environment within the vicinity of the marsh. This method can even work in larger/deeper marshes if the number of aerators necessary is practical.

##### **Salt water and Tidal Marshes**

Spills which occur in these environments allow for varying response options depending upon factors such as size of the marsh, depth, proximity to larger water and current tidal condition. For releases which occur in larger marshes at high water times. Response to the ethanol component is very limited and will most likely be simply to allow the spill to disperse into the larger water and dilute.

If a spill happens during low-water conditions there are more options including those similar to response and clean-up of soil spills. If the low-tide marsh condition leaves pockets of water or a low flow surrounded by wet exposed ground, the ethanol will not

completely disperse providing opportunity to remove it and potential for dangers associated with its flammability. Failure to adequately remove accessible ethanol during the low-water condition will simply allow it to dilute and impact more water once tidal levels return. Thus, it is imperative to address the spill while tidal conditions leave it exposed. Methods in this case can include pumping water/ethanol mixture from isolated pockets; applying sorbents designed to pick up water soluble liquids over exposed areas, and controlled burning of the material.

### **7.2.5 Marine Areas**

Ethanol and blends spilled into salt-water environments will behave in essentially the same manner as in fresh-water incidents. Ethanol is still highly water soluble in salt-water and it can also consume dissolved oxygen very quickly. Even in marine environments BTEX components of the denaturing additive will separate and must be dealt with differently. Options are very limited and decrease with the size of the water body and its proximity to open ocean.

#### **Inner Harbor**

A release which occurs in the calmer and less current influenced waters of an inner harbor allows a more targeted response. As in fresh-water systems, any gasoline components will float and can be controlled with booms and removed by skimming if required. The ethanol will enter solution rapidly and also consume dissolved oxygen as it either assimilates into the water or follows whatever currents are present. Since removal of the alcohol from a large water body is almost impossible, the only options available include 1) letting the material dissolve and disperse and 2) supplementing dissolved oxygen by means of barge mounted air compressors and lengths of perforated pipe. This proved effective and restored dissolved oxygen values to habitable levels in the Kentucky River several years ago following a massive bourbon spill.

#### **Outer Harbor**

A spill which occurs in the outer harbor areas will be more difficult to respond to, especially in dealing with the ethanol component. Outer harbor zones are deeper and contain stronger currents. Recovery of the BTEX component if the material was denatured with gasoline can be accomplished via booms and skimming. The ethanol will quickly dissipate in currents and is virtually impossible to control. Addition of dissolved oxygen is difficult as the “dead zone”, if present, will be guided by currents and may even be confined to certain depths within the thermocline.

## **Open Ocean**

There are no real response options in the open ocean. The deeper waters, stronger currents and larger waves will serve to quickly dilute the material and make any sort of recovery or dissolved oxygen supplementation virtually impossible. Any response efforts should be focused on the gasoline components, if present, and any fuel oil released from the craft involved.



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## *Appendix A*

### *Case Studies*

# LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS



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## **A1. INTRODUCTION**

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Although ethanol has been produced and transported in large volumes for several decades there have been relatively few incidences involving its catastrophic release into the environment. There have been several occasions of underground storage tanks containing ethanol fuel blends leaking, some for very long periods. These have involved E-10 type fuels which are not the focus of this report.

Most of the high-concentration ethanol is moved from production plants to blending terminals by rail. In fact, the majority of the event data is from rail incidents, several of which will be discussed in detail. The other well-documented sources of ethanol impact to the environment have been the result of fire incidents at distilleries. Two very significant events occurred in Kentucky in 1996 and 2000. This section summarizes incidents that have occurred involving ethanol. In many cases, the information presented lacks detail due to the very limited information available.

## **A2. RAILROAD INCIDENTS**

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Recently, with the rise of many more corn to ethanol plants across the Midwest Corn Belt, railroad incidents involving ethanol have begun to occur. Trains can carry upwards of eighty 30,000 gallon capacity tank cars. Even so, considering the amount of ethanol which travels over the nation's rails, there have been only a few major incidents and the environmental impacts have been limited in the majority of these, primarily due to the resulting fires consuming most of the material.

### ***New Brighton, PA***

On October 20, 2006 an eastbound Norfolk Southern train derailed consisting of eighty 30K gallon tank cars of 95% ethanol denatured with gasoline. The incident occurred at approximately 10:30 pm and while the train was traversing the bridge over the Beaver River just west of the city of New Brighton. A total of twenty-three (23) tank cars derailed. Three cars ended up in the river and the other twenty were scattered along the bank and the rails at the eastern end of the bridge with approximately 17 being compromised.

There were fortunately no deaths or injuries. The resulting explosion and fire warranted the evacuation of all persons within a several block radius, which amounted to approximately fifty people since the incident occurred in a largely commercial section of town. The fire was controlled and then allowed to burn itself out. This action consumed the bulk of the material and

limited release to the soil and water. The three cars which actually entered the river were not punctured and the product did not leak from them in any significant quantity.

The fire consumed most of the product and although an estimated 60,000 gallons may have entered the river there was little impact on the environment noted. The Beaver River is a large and fast flowing (18,000 cfs at the time) system and no fish kill or any other impact was noted. Trace levels of ethanol and gasoline components were detected downstream of the site. The nearest public drinking water supply intake was located 11 miles downriver and was not impacted from the spill.



Figure 1. View of derailment. NS train 88QB119 was traveling from left to right.

### ***Painesville, Ohio***

On October 10, 2007 approximately 30 cars of a CSX train derailed outside Painesville, OH. Of



the thirty cars that left the tracks, five were tankers containing denatured ethanol. The other cars contained bio-diesel, phthalic anhydride, and butane. Several of the ethanol cars exploded and burned. Fire fighters used copious amounts of water to cool the butane car and the resulting run-off carried spilled ethanol into a nearby stream.

The fire burned for three days. The stream was dammed and pumped to

remove approximately 500,000 gallons of impacted water for disposal. When it became evident that ethanol had impacted a second stream it was aerated to minimize the loss of dissolved oxygen. Samples were collected from the streams and the nearest outlet stream. In addition, water quality checks were performed on a regular basis at locations along both impacted streams and their outlets. Visibly impacted soils from the area of the derailed cars were removed and samples collected.

No long-term or adverse effects were noted following the actions taken.

### ***Luther, Oklahoma***

In August 2008 eight cars of 110-unit train derailed in central Oklahoma, outside the small rural community of Luther, OK. Seven of the cars were tank cars containing denatured ethanol or crude oil. The resulting explosions and fire forced evacuation of all persons within a 1-mile radius of the incident. There were no injuries or deaths. The fire was allowed to burn itself out and there was minimal environmental impact.

### ***Rockford, Illinois***

On June 19, 2009 14 tank cars of denatured ethanol derailed while traversing a crossing near the city of Rockford, IL. Twelve of the tanker cars caught fire, and one motorist was killed and nine others injured from the resulting explosion and fire. Approximately 600 homes were evacuated and the fire was allowed to burn itself out, which took approximately 24-hours. Approximately 360,000 gallons of ethanol were consumed in the fire, and 55,000 to 75,000 gallons released in soil and unnamed creek. The unnamed creek is a tributary to the Kishwaukee River, which drains into the Rock River.

Approximately 1400 tons of soil were removed from the site, and runoff water was controlled. A nearby drinking water supply was also sampled, with no ethanol detected. Air monitoring was conducted at the site and surrounding community from June 21 through July 2, and no elevated volatile organic compound concentrations were identified.

On June 20, a fish kill was observed on the Rock River over a 50 mile area. This area is about 35 miles downstream of the spill location, and has not definitively been related to the spill. Surface water sampling was initiated on June 21 in the unnamed creek, and the Kishwaukee and Rock Rivers, but ethanol was not detected (EPA 2009). Dissolved oxygen levels were determined to be normal, although the time of sampling was not specified.

Soil borings and monitoring wells were installed and sampled at the site. In addition, several private wells in the area were sampled. The results for all soil and water samples were either non-detect or below applicable screening criteria (EPA (2009b)). However, the analyses may

have been limited to BTEX and Total Petroleum Hydrocarbons (TPH) – Gasoline Range Organics (GRO). Fish tissue samples were also analyzed, and both ethanol and acetaldehyde were detected (EPA 2009b).

### ***Knoxville, Tennessee***

On September 15, 2009 five tank cars hauling ethanol overturned in Knoxville, TN. The derailment occurred while the train was slowing to off-load and as a result no fire resulted. Approximately 6000 gallons of ethanol are believed to have been released from the two cars that were compromised. Approximately 1000 gallons were recovered from visible pools once the cars were up-righted.

### ***Arcadia, Ohio***

On February 6, 2011 at approximately 2:15 am, a Norfolk Southern train with 62 tank cars all loaded with denatured ethanol (95%) derailed approximately one and a half miles outside the village of Arcadia, OH. Thirty-four of the cars derailed and two immediately exploded and burned. Thirty-two others became involved due to the heat. Two cars were intact and later transferred to semi tankers and reloaded on train cars to be delivered. Local volunteer fire-fighting crews concentrated on the safety of nearby residents, preventing access to the area. Numerous fire departments staged in Arcadia in the event it was determined that protection of a nearby Farmers Co-op was needed. First-responder actions concentrated on evacuation of approximately 20 houses and maintaining a secure perimeter. The fires were essentially allowed to burn, involving other cars within the crash pile for several hours. Once the major fires had subsided sufficiently to permit site entry, railroad salvage workers began to separate uninvolved cars.

Fire-fighters shuttled water to the scene using 7 tankers, and supplied a continuous source of water to the environmental and railroad salvage crews. The environmental and railroad salvage crews foamed the inside of the cars to extinguish the fire and applied cooling waters to the exterior of the cars before they were emptied by vac trucks which were off loaded to frac tanks until the material could be shipped off site. Once the cars were cooled that were removed from the accident zone. It is estimated that 80% of the foam was contained within



Arcadia Spill  
Source: OhioEPA

the tank cars. Salvage and product removal operations continued for several days with the last burning car extinguishing by late Monday evening. The tracks were replaced and re-opened by Tuesday afternoon. An estimated 780,000 gallons of denatured ethanol were either burned or spilled in the incident. Relevant response approaches and observations are summarized below:

- During the response, air-monitoring was conducted primarily for BTEX using portable PID systems. Ethanol was not directly monitored other than through LEL readings.
- Product and cooling water spilled onto the track area, onto two tiled farm fields bisected by the tracks and into a small bar ditch located below the tracks and a storm catch basin directly under the derailment site. Cooling water potentially mixed with denatured ethanol also entered a storm drain located at the Co-op. Both the storm water drain and creek empty into the South Branch of the Portage River.
- The creek was first dammed approximately half a mile from the derailment to protect this resource and to allow recovery operations to proceed along the creek. Due to the weather conditions, the creek was frozen which caused the ethanol to migrate downstream under the ice. A second dam was placed approximately a mile from the derailment and ahead of the migrating ethanol. As the ethanol migrated downstream it melted the surface ice and open pools were seen along the creek. The liquid was vacuumed from the creek in three locations and transferred into fractionation tanks for off-site disposal. Vacuuming continued for several days until the melt and rains made it impossible. By that time aeration systems had been placed in the creek at three locations and activated carbon was en route to be staged near the dams. The dams remain in place and aeration of the creek is continuing at the time of this report. Pools of water onsite continue to be collected due to high levels of ethanol.
- No visible fish kill was noted. Soil remediation actions did not commence until all of the cars were removed from the tracks and are continuing at the time of this report. These consist of removal of visibly impacted areas and post removal sampling.
- Preliminary analysis showed there to be approximately 10 mg/l of benzene in the drainage water, which is 2000 times the Ohio drinking water standard of 5 ug/l. Ohio EPA directed that collection and testing continue until the drainage water meets the 5 ug/l benzene limit. Those actions were continuing at the time of this report.



- State and Federal environmental agencies directed sampling for BTEX and ethanol in soils. Benzene was determined to be the site action-level driver, as there is no clean-up level for ethanol defined in Ohio regulations. Ethanol concentrations were determined



for informational purposes only. In the creek and South Branch of the Portage River samples were collected and analyzed for BTEX, ethanol, and water quality parameters including biochemical oxygen demand, chemical oxygen demand, and dissolved oxygen. Residents' groundwater wells were also sampled for ethanol and BTEX. No groundwater samples indicated impacts.

### A3. DISTILLERY INCIDENTS

Aside from incidents in transport of fuel ethanol, large volumes of ethanol have entered the environment as a result of distillery fires. Two incidents in Kentucky were found. The first in 1996 occurred at the Heaven's Hill's Distillery in Bardstown, KY. In the case of this fire the location of the buildings, distance from a water body, and intensity of the fire limited the environmental impact. This particular fire occurred during a very windy day (55 mph winds) and as such, a total of seven storage/aging buildings, each holding 900,000 gallons of bourbon and thirteen other buildings were destroyed. However, the intensity of the flames and the terrain caused more pooling and burning of the liquids and limited damage outside the fire zones. The second incident, at the Wild Turkey Distillery in Lawrenceburg, KY did not result in the same limited impact to the environment.

#### ***Wild Turkey Distillery-Warehouse K Fire.***

On the afternoon of May 7, 2000 workers at a nearby water treatment plant noticed flames coming from a bourbon storage/aging building known as Warehouse K. Warehouse K was situated at the end of a long line of similar buildings and on the edge of the distillery property overlooking the Kentucky River. It was constructed of slat board siding and a tin roof and stored approximately 17,300 53-gallon barrels of 107-112 proof bourbon whiskey. It was also designed to collapse onto itself in the event of fire which it did. By the time fire-fighters arrived, the building was totally involved and the crews concentrated on protection of nearby structures and worker safety, essentially allowing Warehouse K to burn its self out. Upon arrival, fire-fighters noted that a flow of burning bourbon was traveling down a wooded hill and into the river below.



They concentrated on protecting the other distillery structures and controlling any spot fires in the woods, but did not block the flow of burning alcohol.

Once it was discovered that alcohol was indeed entering the river, at a point upstream of the city of Lawrenceburg's drinking water plant intake, the plant was shut down to keep the alcohol from entering the treatment process. Fire-fighters then used shuttle tankers filled in the river to bring cooling/protection water to the fight. The fire burned and cooling/protection activities continued through the night. The city water plant was back on line within 24-hours.

Initial assessment from the state environmental agency was that the incident had resulted in limited impact to the environment and that possibly 20-percent of the alcohol had actually entered the river. State officials figured that this volume (approximately 200,000 gallons) would have limited impact on a large river system such as the Kentucky River. A couple of days later, the morning of May 11<sup>th</sup>, the city of Frankfurt, located 14-miles downstream from the site reported a sweet smell in the river and a massive fish kill. Other reports soon followed in what would be the largest chemical spill induced fish kill in the history of the state. At its peak the area of "dead water" stretched five to six miles in length and traveled approximately five-miles per hour downstream.

Officials were surprised that the movement of the material through the various locks and dams did not serve to eliminate the alcohol and aerate the water. On May 18<sup>th</sup>, when it became obvious that the zone of dead water was not subsiding, EPA began to oxygenate the dead water area as it reached the confluence of the Ohio River. They did this by using six barges equipped with air-compressors connected to lengths of perforated pipe. Aeration continued until dissolved oxygen levels reached at least 5 ppm, and ended on the 25<sup>th</sup> of May.

## ***A4. Marine Incidents***

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The Coast Guard monitors ethanol spill statistics. They reported (USCG 2010) that there have been only two ethanol spills over the last six years while loading or discharging, and both were less than five gallons. They also report that waterfront facilities have averaged one spill a year, but only one of these was over 100 gallons.

Below are the descriptions of two documented incidents from marine transport of ethanol and ethanol blends. One occurred in the open ocean (not included in statistics above), and the other during on-loading activities in port. In both instances no response actions were targeted to the ethanol itself.



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### ***Bow Mariner Incident***

On February 28, 2004 a chemical tanker *Bow Mariner*, exploded and sank approximately 50 miles off the coast of Virginia. At the time she was carrying 3.5MM gallons of ethanol in 10 full cargo tanks. The USCG investigation (USCG 2005) determined that the explosion was actually due to the empty tanks, which had previously contained another volatile and flammable gasoline additive, MTBE, had not been inerted after off-loading, and were opened while at sea. The explosion caused massive rupturing of the entire cargo deck and the ship sank in approximately two hours. Six crewmen were rescued, three bodies recovered and eighteen crewmen lost and never recovered. Although environmental response actions were required, they focused entirely on the fuel oil that was released from the ship's tanks. In fact, ethanol was considered non-regulated and not addressed in any way during the response.

### ***Harbor On-loading Incident***

On January 11, 2010 a chemical tanker, *Sichem Defiance*, was on-loading a cargo of 55,000 barrels of ethanol while in port at New York Harbor. Operators failed to properly monitor the on-loading process and over-filled one of the ship's cargo tanks to the point of rupture. The rupture collapsed a portion of the upper deck, but did not release material into the harbor.

## ***Appendix B***

### ***Fate and Transport Literature Review***



## **B1. INTRODUCTION**

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This appendix provides a review of the fate and transport of ethanol in soil, ground water, surface water and the atmosphere. The information provided here is presented in summary form in Section 4. This review uses information from numerous sources, including peer-reviewed literature, industry publications, and agency presentations.

## **B2. NEAT VERSUS E-BLEND SPILLS**

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The New England Interstate Water Pollution Control Commission (NEIWPCC, 2001) report summarizes the fate and transport issues associated with a release of neat ethanol into the environment and compares them with the issues related to ethanol blends. A spill that releases large volumes of neat or denatured ethanol into the environment, such as an accident involving a unit train or a marine tanker carrying ethanol, or an accident at a bulk ethanol storage facility, would result in a large surface spill migrating rapidly over the land surface. This spill would eventually reach a surface water body such as a pond, stream, river or the ocean; or it may infiltrate into the soil and reach the groundwater. In comparison, E-blend releases, such as E10 or E85, are expected to be smaller in volume, as these releases often occur during splash blending of ethanol with gasoline, tanker truck accidents, or at retail gasoline stations. Unlike gasoline spills, the sampling and analysis of ethanol following E-blend releases have been limited. Some studies have indicated that the presence of ethanol in gasoline can inhibit BTEX (benzene, ethyl benzene, toluene, and xylenes) biodegradation in groundwater systems, resulting in enhanced BTEX plumes (Powers et al., 2001; Deeb et al., 2002). In contrast, other studies have suggested that the presence of ethanol in gasoline can reduce the persistence of benzene in E-blend releases due to increased biomass growth facilitated by the ethanol (Gomez and Alvarez, 2009).

## **B3. GENERAL DISCUSSION OF IMPORTANT FATE PROCESSES**

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This section describes some of the important fate processes that affect ethanol in the environment, including biodegradation, partitioning and methane production. The following sections (4.0 through 7.0), discuss fate and transport processes by medium.

### **B3-1 Ethanol Biodegradation**

Howard et al. (1991) and NEIWPCC (2001) indicate that ethanol undergoes biodegradation at a rapid rate in the atmosphere, soil, surface water and groundwater if there are sufficient levels of

electron acceptors and nutrients available to degrade the ethanol. Degradation rates of ethanol are higher than gasoline, with half lives ranging from hours to days (Malcolm Pirnie, 1998; HSDB, 2011). Due to the rapid loss of ethanol through photo-oxidation in air and biodegradation in soil and water, ethanol is unlikely to accumulate in the soil, air, surface water, or groundwater. Degradation rates have been estimated using field and laboratory studies; however, there is a great deal of uncertainty as to how these estimated rates of ethanol loss will apply in realistic field conditions. Therefore, rates discussed below are considered to represent order-of-magnitude estimates and may not be applicable for site-specific releases.

Under aerobic conditions, biodegradation of ethanol in fresh and salt water with filtered sewage seed resulted in 5-day theoretical biochemical oxygen demand values ranging from 37% to 86%, at concentrations of 3 to 10 mg/L (HSDB 2011). In a microcosm using sandy aquifer material and groundwater, a half life for ethanol with a starting concentration of 100 mg/L, was reported to be 3 days in samples prepared with 20 mg/L of benzene, toluene or o-xylene under aerobic conditions (HSDB 2011). Using the same microcosm setup, but under anaerobic conditions, the half-life was reported as 1.5 days (denitrifying conditions, and 5 days (iron-reducing conditions).

Further discussion of biodegradation is provided by medium in later sections of this Appendix.

### ***B3-2 Partitioning of Ethanol Between Environmental Media***

Malcolm Pirnie (1998) describes the mechanisms that lead to the partitioning of ethanol between the air, water, and soil media. These mechanisms are summarized in the following sub-sections.

#### **Air/Water Partitioning**

The air-to-water partitioning behavior of ethanol is governed by Henry's Law and described by the Henry's Law constant, which represents the equilibrium ratio of a contaminant's concentration in the air to its concentration in the water. The value of the dimensionless Henry's Law constant for ethanol is approximately  $2.5 \times 10^{-4}$  at 25° C (Malcolm Pirnie, Inc., 1998). This relatively low value of the Henry's Law constant for ethanol indicates that ethanol has a strong affinity for the aqueous phase compared to the vapor phase. As a result, ethanol volatilization from surface water or off-gassing from groundwater are not likely to be significant mechanisms for ethanol mass loss from water. It is noted, however, that the Henry's Law constant is a function of temperature, and that this constant, and the affinity for ethanol to partition into the vapor phase, will increase with increasing temperature.

## Soil/Water Partitioning

The partitioning of ethanol concentration between the soil and water is described by its soil/water partition coefficient  $K_d$ .  $K_d$  values can be estimated by the following:

$$K_d = K_{oc} f_{oc}$$

where  $K_{oc}$  is the partition coefficient for the target species (ethanol) and soil organic carbon, and  $f_{oc}$  is the fraction of organic carbon present in the soil. HSDB (2011) reports a  $K_{oc}$  for ethanol of 1, resulting in low partitioning of ethanol to most soils. This indicates that ethanol will generally migrate with groundwater, and adsorption onto soil or sediment are not likely to be significant fate and transport mechanisms (Wood et al., 1990; Zogorski et al., 1996)..

### ***B3-3 Methane Production***

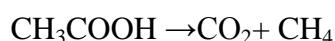
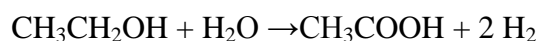
Anaerobic biodegradation of ethanol in groundwater results in the production of methane (API, 2003; Schaefer et al., 2010). The methane may then volatilize from groundwater into soil gas. If the soil gas were to migrate to a confined space, it may lead to an explosion hazard (Jewell et al., 2010)

After an ethanol spill, the following conditions must be met for an explosion hazard to occur from methane (ASTDR, 2011):

- **Methane gas generation.** At most sites, ethanol degradation is expected to be rapid as compared to the ability of groundwater flow to flush ethanol away from the spill location. Methanogenesis will be the dominant degradation pathway and methane will be the dominant degradation product of ethanol (see discussion below). The resulting methane can volatilize into the unsaturated soil (Wilson and Adair, 2007).
- **Methane gas migration.** The methane gas must be able to migrate from soil and groundwater to underground utility pipes, drains, conduits or through natural subsurface preferential migration pathways present in the geologic media.
- **Collection in a confined space.** The methane gas must collect in a confined space to a concentration at which it could potentially explode. A confined space might be a manhole, a subsurface space, a utility room in a home, or a basement. The concentration level at which gas has the potential to explode is called the explosive limit. The potential for a gas to explode is determined by its lower explosive limit (LEL) and upper explosive limit (UEL). The LEL and UEL are measures of the percent of a gas in the air by volume. However, an explosion hazard may exist if a gas is present in the air between the LEL

and UEL and an ignition source is present. For methane, the LEL is 5% by volume and the UEL is 15% by volume. At concentrations below its LEL and above its UEL, a gas is not considered explosive.

The introduction of fuel ethanol to groundwater stimulates anaerobic microbial activity leading to methanogenesis, which is the production of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) by biological processes. The chemistry behind the methanogenesis from ethanol is as follows:



For example, 46 mg/L ethanol can produce 16 mg/L methane (Wilson and Adair, 2007). At higher concentrations (near 1000 mg/L) ethanol rapidly ferments to methane at a rate near 20 to 60 mg/L per day (Jewell, et al., 2010). At an average groundwater temperature of 15°C, and an atmospheric pressure of 1 atm (atmospheres), 0.73 liters of methane gas will be produced per gram of ethanol (Powers et al., 2001).

Methane vapors are produced over an extended period of time and persist in soil gas for a long time, at levels exceeding the lower and upper explosive limits for methane (5% and 15% by volume, respectively (Wilson and Adair, 2007).

The methane originating from the anaerobic degradation of ethanol in groundwater first undergoes aerobic biodegradation in soil pores and consumes the available oxygen from the soil gas (assuming oxygen is initially present). This oxygen would otherwise be available to degrade benzene and other gasoline constituents introduced to soil gas from an E-blend spill. The aerobic degradation of benzene is therefore limited in presence of ethanol. One part methane will consume two parts oxygen. Considering that air is 20% oxygen, the biodegradation of 10% methane by volume can consume all of the oxygen in soil gas and stop the aerobic biodegradation of benzene. The lack of benzene degradation caused by the consumption of oxygen by methane results in increased persistence of benzene in soil gas and poses a fire and explosion hazard (Jewell et al. 2010).

The production of methane, accumulation and potential for explosion is of concern to emergency responders following an ethanol spill. Specific issues of concern are addressed below:

- **Timing of methane generation:** The time elapsed after an ethanol release until methane generation begins, and the rate at which it occurs, will be very site specific. Methane generation typically will not occur until available electron acceptors (i.e., oxygen, nitrate, iron, and sulfate) are consumed. Water with high levels of these compounds prior to



ethanol exposure will typically take longer to generate methane. Waters previously exposed to hydrocarbon or alcohol contaminants might also have higher microbial levels, thus able to more rapidly consume ethanol and generate methane. In laboratory experiments (Schaefer et al., 2010), it took about 6 weeks before methane was generated in anaerobic microcosm experiments. Chen et al. (2008) observed methane generation after about 10 weeks.

Based on these rates, it appears that there is a lag time of 6 to 10 weeks between the ethanol spill and generation of methane. The lag time is adequate for an environmental response to be initiated and actions taken to contain the ethanol spill, recover a large percentage of the spilled ethanol, provide aeration to the waters if necessary, and thereby eliminating the source material for methane production. If these actions are taken, the explosion hazards from methane generation will be minimized.

- **Conditions for enhancing or inhibiting methane production:** Methane is produced by the anaerobic biodegradation of ethanol in groundwater, through the methanogenic reactions. Such reactions do not occur in the presence of electron acceptors (i.e., oxygen, nitrate, iron, and sulfate). In addition, they will not occur in the presence of concentrations of ethanol that are toxic to microorganisms. Once the conditions are suitable for methanogenesis, the reaction rate will depend on environmental conditions, such as temperature.

The general presumption is that at sites with sandy soil, steep topographic gradients (used as indicator of subsurface hydraulic gradients), and presence of nearby surface water bodies to which groundwater may discharge, groundwater is likely to be aerobic and moving rapidly. The potential for methane generation and accumulation of methane in soil gas is lower in such environments. At sites with flat topography, clay, peat or other soils with high organic matter, water logged or swampy conditions, it is expected that groundwater flow is not as rapid and anaerobic conditions favoring the generation of methane may occur. If the ethanol spill occurs in an area where hydrocarbon or alcohol contaminants from previous environmental releases may be present, these areas might also have higher microbial levels, thus able to more rapidly consume ethanol and generate methane as compared to remote areas with no prior contamination history. Anaerobic conditions may also already be present in such areas.

- **Rate of methane production:** The rate of methane generation is related to temperature, and can be conservatively estimated by the ethanol biodegradation rate under methanogenic conditions. Based on Shaefer et al. (2010) and Deeb et al. (2002), the first

order rate constant for ethanol under methanogenic conditions can range from about 0.08 to 0.3 per day while the first order rate constant for methane is in the 0.16 to 0.6 per day range. The corresponding half life of ethane ranges from 2.3 days to 8.7 days; which means that in approximately 2 to 9 days after methanogenic conditions have been reached, half of the ethanol spilled and introduced to the groundwater will be converted to methane. The volumetric rate of methane produced depends upon the dissolved ethanol concentration and the first order rate constant discussed above. There is an upper limit to ethanol biodegradation, and thus methane generation, as a result of ethanol toxicity. Some of the methane produced will be transported in groundwater, while the remainder may escape as soil gas. The accumulation of methane vapors in the subsurface will likely depend upon the rate at which methane vapor escaping from the water (either surface or subsurface) can be dissipated. For surface spills, wind and diffusion will likely prevent any substantial methane accumulation. However, in enclosed areas, in subsurface environments, or where subsurface soil gas can impact things like basements or utilities, accumulation can occur. Providing electron acceptors (oxygen, nitrate, sulfate, etc.) should limit methane generation.

Therefore, while methane will be generated after an ethanol spill, the potential for an explosion hazard is dependent upon the accumulation of methane gas in a confined space to a potentially explosive concentration. As discussed previously, the potential for a gas to explode is determined by its LEL and UEL (5% and 15% by volume), respectively, measured as the percent of gas in the air by volume. An explosion hazard may exist if a gas is present in the air between the LEL and UEL and an ignition source is present. For methane, the LEL is 5% by volume and the UEL is 15% by volume. Powers et al. (2001) indicate that after an ethanol spill, at an average groundwater temperature of 15°C and an atmospheric pressure of 1 atm, 0.73 liters of methane gas will be produced per gram of ethanol. The methane gas is produced over an extended period of time and will persist as soil gas for a long time, at levels exceeding the LEL and UEL (Wilson and Adair, 2007). If this soil gas is vented to the atmosphere, an explosion hazard is unlikely to exist; however, the confinement of the methane in soil gas in subsurface structures like a manhole, a subsurface space, a utility room in a home, or a basement could lead to an explosion hazard.

- **Empirical data from large volume ethanol spills:** Empirical data regarding the persistence of ethanol-generated methane in soil and groundwater was collected at a bulk fuel terminal in the Pacific Northwest, where 19,000 gallons of neat ethanol were released from an above ground storage tank in 1999 (Buscheck et al. 2001). High ethanol concentrations (exceeding 20,000 ug/L) were measured at distances over 250 feet

downgradient from the spill location. The groundwater velocity in the spill area was estimated to range from 300 to 400 feet per year. Within three months of the spill, ethanol concentrations in groundwater of up to about 16,000 mg/L were measured. Groundwater concentrations declined dramatically, and by July 2001 ethanol was not detected in the two wells that previously had the highest concentrations.

The degradation of ethanol resulted in strongly anaerobic conditions in groundwater following the spill. Oxygen, sulfate, and nitrate levels were depleted within the ethanol plume. Unfortunately, these parameters were not measured until 15 months after the spill occurred. Dissolved methane concentrations in groundwater at that time ranged from about 5,000 to 10,000 ug/L, but a year later (June 2001), had increased to over 30,000 ug/L, approximately 27 months after the spill. During the same time frame, ethanol concentrations in source area groundwater were declining, indicating the progression of anaerobic degradation of ethanol and the production of methane. A soil gas survey was conducted in June and July 2001 (27 months after the spill). Methane concentrations in excess of the upper explosive limit were detected at 4 feet below grade in the areas of the highest dissolved methane concentrations in groundwater.

Tousignant and Evrard (2009) also reported the results of a spill of approximately 27,000 gallons of denatured ethanol (containing 2% to 5% gasoline) as a result of a rail collision between Montreal and Ottawa, Canada on May 2, 2005. Impacted surface soil was removed (12 inches), however, the spill resulted in impacts on groundwater. Surface application of a quick reacting oxidizer (Regenox<sup>TM</sup>) was initiated to reduce ethanol levels (toxic to bacteria) at the spill location (July 2006). Additional treatment consisted of surface application of a slow release oxidizer (ORC advanced<sup>TM</sup>) at the spill location (September 2006), application of ORC down-gradient of the spill location in infiltration/interception trenches (November 2006), and ORC injection to groundwater in the plume area to treat BTEX contamination (August 2008). Concentrations of ethanol in the source area were as high as 46,000,000 ug/L, but were reduced to non-detect in all locations by February 2008. BTEX compounds were more persistent, even with the ORC application, substantiating the longer half lives of BTEX compounds and therefore slower degradation rates as compared to ethanol. The authors observed methane in groundwater, but its generation was likely inhibited by the addition of oxidizers. Methane was also observed in some non impacted wells. The authors attributed this observation to the degradation of ethanol by-products, but may have been a result of the continued migration of methane in groundwater.

- **Extent of methane related hazards:** The empirical data from Buscheck et al. 2001 suggests that methane related hazards will extend to the area occupied by the ethanol plume in groundwater, and will extend to a distance that can be estimated from the groundwater velocity and the time since the release. The extent of the groundwater plume will provide the upper bound for the extent of methane impacts, except for any preferential pathways such as utilities that may provide further spread of the methane in soil gas. Numerical estimates of the ethanol plume impacts can be made using software such as FOOTPRINT (EPA, 2008). In general, for most spills, the ethanol in groundwater is expected to be degraded and not be of concern in a year or two (Wilson and Adair, 2007).

## ***B4. FATE AND TRANSPORT IN SOIL***

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As previously discussed, neat ethanol or E-blend fuels can infiltrate into the subsurface. The liquid will then percolate through the subsurface vadose zone soils, moving through the gas-filled pore spaces, until it ultimately reached the water table. Due to its affinity to reside in the water phase, migrating ethanol will partition into soil moisture; this partitioning can slow the downward migration of ethanol (McDowell and Powers, 2003). Dissolved ethanol present in soil pore water typically is subject to biodegradation, which can further attenuate the rate of ethanol migration to the water table.

The Lawrence Livermore National Laboratory (LLNL, 1999) report discusses how the presence of ethanol in E-blend fuels affects the migration and distribution of gasoline in the unsaturated zone by reducing the capillary forces and altering the pore structure of some minerals. In the presence of ethanol, gasoline components can enter smaller pore spaces and drain more easily from unsaturated zone soils. At bulk terminals and other locations where unsaturated-zone hydrocarbon contamination may pre-exist, the introduction of ethanol may mobilize the existing contamination. The depth and the area of hydrocarbon pool on top of the water table may be altered by the presence of ethanol which reduces the capillary forces and therefore reduces the height of the capillary fringe.

## ***B5. FATE AND TRANSPORT IN GROUNDWATER***

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Once ethanol reaches the groundwater, its fate and transport is governed by the groundwater flow rate and natural attenuation processes such as biodegradation, adsorption, dispersion and the partitioning of ethanol between soil, water and air. Biodegradation is the primary mechanism for the loss of ethanol from the groundwater system. The aerobic and anaerobic degradation of

ethanol mechanisms were previously discussed in Section 3.1, while the attenuation caused by adsorption and partitioning of ethanol among various media was discussed in Section 5.2 of this Appendix. Although there are non-toxic intermediate byproducts of ethanol degradation such as acetate and hydrogen gas, the final product of aerobic degradation of ethanol is carbon dioxide, while ethanol degrades anaerobically to yield methane and carbon dioxide.

Unlike the standard components of gasoline which are hydrophobic, ethanol is hydrophilic. The LLNL (1999) report and NEIWPC (2001) identified the following characteristics of ethanol and E-blend fuel fate and transport in groundwater:

- Ethanol degrades rapidly when released to the environment under favorable conditions;
- The presence of ethanol in E-blend fuels will affect the dissolved concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) in groundwater if the ethanol concentrations are high;
- The presence of ethanol in E-blend fuels will increase the residence time of fuel hydrocarbons in the groundwater;
- The presence of ethanol in groundwater will increase BTEX plume lengths, from 1.1 up to 2.5 times farther than without ethanol. This is because ethanol alters the processes of sorption and retardation of gasoline components in groundwater and its biodegradation reduces the rate of BTEX biodegradation. Some studies (Gomez and Alvarez, 2009) suggest that ethanol may actually enhance the rate of benzene biodegradation, thereby reducing benzene plume length and persistence;
- If spilled as a neat product, ethanol can remobilize the gasoline components of pre-existing contaminant plumes and cause lateral spreading of liquid petroleum and 10-fold increases in the concentration of BTEX; and
- The introduction of ethanol may affect aquifer porosity and hydraulic conductivity due to bio-film growth, mineral precipitation or dissolution, and nitrogen or methane gas generation.

When ethanol is introduced to groundwater as an E-blend fuel, the behaviors of water and the E-blend fuels change as follows (LLNL, 1999):

- Ethanol partitions preferentially into the aqueous phase;
- Solubilities of gasoline hydrocarbons in water increase;

- Solubility of water in gasoline increases; and
- Interfacial tension between the water and the gasoline phases is reduced.

## ***B6. FATE AND TRANSPORT IN SURFACE WATER***

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After a large volume surface spill, neat ethanol or E-blend fuel will flow over pavement and soil until reaching a point of discharge into storm sewers, wetlands, lakes, and streams. During the overland flow over soil and pavement, ethanol will partially volatilize into the atmosphere. As the ethanol flows over soil, some of the ethanol will infiltrate the soil and reach the groundwater, which may discharge to a surface water body. The remaining ethanol could reach a wetland or a surface water body directly. Upon reaching a surface water body, either as groundwater discharge or surface flow, ethanol will rapidly mix with the water and go into solution (Malcolm Pirnie, 1998).

As discussed above, due to the low  $K_{oc}$  for ethanol, ethanol in surface water is not expected to partition onto suspended solids or sediment (HSDB 2011). Also as discussed above, volatilization from surface water is not expected to be a significant fate and transport mechanism. HSDB (2011) identified a bioconcentration factor (BCF) for ethanol of 3, indicating it has a low potential for accumulation in aquatic organisms.

The primary fate and transport mechanism in surface water is expected to be biodegradation. With concentrations greater 10°C, Malcolm Pirnie (1998) reported half lives ranging from hours to days.

## ***B7. FATE AND TRANSPORT IN THE ATMOSPHERE***

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Malcolm Pirnie (1998) reported that the half life of ethanol in the atmosphere is in the order of days, especially in summer when ethanol undergoes rapid reactions with hydroxyl radicals.



## *Appendix C*

### *Health Effects Literature Review*

# LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS



JULY 2011



## **C1. INTRODUCTION**

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This appendix provides a review of health effects of ethanol, which is summarized in Section 5.0 of the report. This review uses abstracts and reviews to the extent possible, as well as original studies where available. The focus of this review is on inhalation exposures, with a limited discussion of ingestion exposures. There is a large body of literature on the effects of alcohol consumption on human health. This is not discussed in detail here, as exposures of this magnitude and duration would not be expected in a spill situation. This review includes discussions of uptake and metabolism, acute toxicity, chronic toxicity, teratogenicity, developmental/reproductive effects, and carcinogenicity.

## **C2. Uptake and Metabolism**

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Ethanol is completely absorbed orally, and about 60% is absorbed via inhalation (NHDES 2009). CIREP (2008) reports that absorption of ethanol occurs through the skin, but doesn't affect the skin barrier, or result in very high internal concentrations. However, they also report that ethanol can enhance the absorption of other substances through the skin.

Nadeau et al. (2003) reported that absorption of ethanol from the lungs was about 75% upon exposure to ethanol in air for six hours at 1000 ppm, somewhat higher than that reported by other authors. They found that ethanol concentrations in expired air reached steady state after three hours of exposure.

Hardman et al. (2001) reported that most ethanol (90% to 98%) is metabolized primarily in the liver to acetaldehyde (the rate-limiting step), and subsequently to acetate and ultimately to carbon dioxide and water. The balance is excreted as unoxidized ethanol in urine, sweat, and expired air. They reported that the oxidation of ethanol by a 70 kg person occurs at the approximate rate of 120 mg/kg per hour. Bingham et al. (2001) reported that at an ethanol air concentration of 8000 ppm and a ventilation rate of 15L/min, the rate of alcohol uptake was equal to the rate of metabolism. Based on review of the literature, EPA's (1997) recommended ventilation rates for short term exposures of adults range from 7 L/min for adults at rest to 53 L/min for heavy activity. Bingham et al. (2001) concluded that a continuous rise in ethanol concentrations in blood would not result from exposure to 1000 ppm in air (Bingham et al. 2001). This conclusion is consistent with that reported above by Nadeau et al. (2003).

Acetaldehyde is largely metabolized by aldehyde dehydrogenases (ALDHs) in the liver. ALDH activity is reduced in the liver of alcoholics. In addition, some individuals, primarily of Asian

descent are deficient in ALDH, making them at higher risk of esophageal cancer (Baan et al. 2007).

### **C3. ACUTE EXPOSURE**

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NEIWPCC (2001) identifies an odor threshold for ethanol of 100 ppm in air. Ethanol vapors cause irritation of mucous membranes of eyes and respiratory tract at concentrations of 5000-10,000 ppm, although such effects were not observed at concentrations less than 5000 ppm (Lester and Greenberg, 1951). Stupor and sleepiness have also been observed at these concentrations (Lester and Greenberg 1951). More severe effects were observed at concentrations of 16,000 to 21,000 ppm. Headaches and other initial signs of intoxication were reported in humans exposed to concentrations greater than 3000 ppm for 2 hrs (OEHHA 1999).

Nadeau et al. (2003) evaluated neuromotor effects (reaction time body sway, hand tremor and rapid alternating movements) in healthy males exposed to 0, 250, 500, and 1000 ppm ethanol in air for six hours. Ethanol was not detected in blood or alveolar air at exposures up to 500 ppm, but at 1000 ppm, blood and alveolar air were 0.443 mg/100 ml, and 253.1 ppm, respectively. Neuromotor tests did not show conclusively significant differences between the exposed and control conditions.

Narcosis, ataxia and incoordination were observed in animals after exposure to 4000-10,000 ppm for 8 hrs (Hobbs et al. 1996). Exposure of rats or mice to 20,000 ppm of ethanol resulted in performance effects, although the lowest dose (12,000 ppm) had marginal effects. The alcohol blood level of rats exposed to 16,000 ppm was 0.05 % - the point at which decrements in human performance have been most clearly documented. Inhalation of 10,000-30,000 ppm for eight hours or more is lethal to rats (HEI 1996). Inhalation of 10,000-30,000 ppm for extended periods (8 hrs or more) is lethal to rats. Ingestion of ethanol has caused death in humans, but OEHHA (1999) concluded that a lethal dose by inhalation was unlikely (OEHHA 1999).

Pastino et al. (1997) developed a pharmacokinetic model for ethanol uptake by inhalation in rats and mice. They concluded that after exposure to 600 ppm ethanol for six hours, maximum blood ethanol concentrations were less than 10% of the concentration reported as the threshold for behavioral effects.

NEIWPCC (2001) concluded that overall data from human studies suggest a threshold for acute neurological effects in blood alcohol range of 0.01-0.05%. Acute ingestion of about 1 g/kg alcohol approximates 0.1% blood alcohol levels, suggesting a 0.1 to 0.5 g/kg as the lowest human observable adverse effect level (LOAEL) for acute ethanol neurotoxicity in humans.

Gleason et al (1969) summarized the following effects associated with blood alcohol levels:

- 0.05-0.15% - decreased inhibitions, incoordination, slow reaction time, blurred vision;
- 0.15-0.3% definite visual impairment, slurred speech, hypoglycemia, and staggering;
- >0.3% marked incoordination, stupor, hypoglycemia, convulsions, coma, and death; and
- 0.18-0.6% - lethal blood alcohol concentrations.

Effects on laboratory animals appear to occur at similar ethanol doses, and with similar symptoms. Ethanol doses of 0.1-0.5 g/kg resulted in increased motor activity in rats and increased aggressiveness in monkeys. At higher doses, incoordination was observed (HEI 1996).

Acute lethal doses in dogs range from 3-10 g/kg, with death resulting in respiratory failure and death within 12 hrs (Reese and Kimbrough 1993). The oral LD<sub>50</sub> for adult rats (lethal dose to 50% of the population) ranges from 11.5 to 17.8 g/kg, while younger rats were more sensitive (LD<sub>50</sub> of 6.2 g/kg) (OEHHA 2000).

## **C4. CHRONIC EXPOSURE**

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### ***C4-1 Subchronic and Chronic Effects***

Most of the literature on chronic exposure of ethanol is related to alcohol abuse. OEHHA 1999 reported that chronic exposure to ethanol results in adverse effects on the liver in animals and humans. Symptoms include fat accumulation and inflammation progressing to focal necrosis and fibrosis. Oral doses initiating these effects were 8-15 g/kg/day in rats and dogs. In humans, alcoholic hepatitis and cirrhosis have been observed with chronic ingestion of 2 g/kg/day (HEI 1996). Toxic effects on the heart, such as inflammatory and degenerative changes have also been observed (NEIWPCC 2001). Severe effects on the heart, central nervous system, and liver have been reported after long term high level exposures, although no thresholds for such severe effects are available (NEIWPCC 2001).

NEIWPCC (2001) reported the results of several researchers that identified effects of chronic exposure (generally oral) to ethanol on blood cellularity and function, particularly white blood cells (Malik and Wickramasinghe, 1986 and Marietta et al. 1998), although the effect of these changes on immune function is unclear. NEIWPCC (2001) indicated that the dose response data is limited in such studies, and it is unclear whether such effects are relevant to low environmental exposures.

One study (Chu et al. 2005) considered the effects of inhalation exposure of rats to ethanol and gasoline separately, as well as combined. They exposed rats to 6130 ppm ethanol, 500 ppm

gasoline, and 85% ethanol gas (6130 ppm ethanol and 500 ppm gasoline) for 6 hours per day, five days per week for four weeks. They found that female rats treated with the mixture showed growth suppression, which was reversed after four weeks in filtered air. They also observed increased kidney weight and liver effects, including increased liver weight and enzyme activity, with the most significant effects associated with gasoline exposure. Combined exposure resulted in additive effects on growth suppression. While other researchers have identified inflammation of the upper respiratory tract with acute ethanol exposures of this magnitude, Chu et al. (2005) observed this effect only with combined exposure suggesting irritating effect when combined. They concluded that inhalation of ethanol and gasoline at the concentrations tested resulted in mild, reversible, biochemical hematological and histological effects, with some indications of interactions when combined.

### ***C4-2 Reproductive and Developmental Effects***

Nelson et al. (1985) administered ethanol to rats at 20,000, 16,000, 10,000, and 0 ppm in air for 7 hrs/day on Days 1-19 of gestation. Maternal weight gain and feed intake decreased during the first week of exposure at 20,000 ppm, and dams were completely narcotized at the conclusion of exposure. They reported no definite increase in malformations at any level of ethanol exposure, although incidence at the highest exposure level was “borderline” significant. They evaluated skeletal, visceral, and external malformations. They concluded that at maternally toxic concentrations (20,000 ppm), ethanol was only possibly teratogenic, and lower concentrations were not teratogenic.

NEIWPCC (2001) indicated that there are some studies in humans and rodents that support ethanol induced genetic effects resulting from moderate to high levels of ethanol exposure (Froines et al, 1998). Findings have related ethanol exposure to chromosomal abnormalities in miscarried pregnancies and sperm, and dominant lethal mutations in mice and rats. They suggested that the mechanism may involve exposure to acetaldehyde as well as ethanol. (Froines et al. 1998) also reports that a variety of studies have shown that exposure of prepubertal rats and mice are exposed to ethanol can result in delays development of male reproductive tract, although dose response data are insufficient to identify specific effects.

OEHHA (1999) reported that rats and mice on liquid diets of 5-10% ethanol for 5 or more weeks showed adverse effects on the testes. They also identified that some studies show effects on the fetus, including growth retardation, malformations, and death in rats and mice fed diets comprised of 15-35% ethanol (by calories). However, other studies showed no effects on mice and rabbits given drinking water containing 15% ethanol.

Human fetal alcohol syndrome is a well known result of alcohol abuse during pregnancy (OEHHA 1999). Effects observed include retardation of growth and development, physical malformations, and behavioral and cognitive problems. In addition, more subtle neurological changes in fetuses have been observed, such as performance on neuropsychological tests, hyperactivity, and lowered intellectual capacity (HEI 1996). HEI (1996) suggested a threshold for fetal alcohol effects of 0.5 oz per day (about one drink per day or 0.2 g/kg/day) for most neurological endpoints, based on the work of Jacobson et al. (1996). They also concluded that this threshold is supported by animal data. Neuromotor effects were observed in monkeys at 1-3 g/kg/d, and some effects occurred at maternal doses of 0.25 g/kg/day (HEI 1996).

### **C4-3 Cancer**

In 2007, the International Agency for Research on Cancer (IARC) reassessed the carcinogenicity of alcoholic beverages. The results of their evaluation are provided in WHO (2010), and summarized in Baan et al. (2007). The conclusion of this evaluation was that alcoholic beverages and ethanol in alcoholic beverages are “carcinogenic to humans”, or Group 1. This category is selected when there is sufficient evidence of carcinogenicity in humans. They concluded that “occurrence of malignant tumours of the oral cavity, pharynx, oesophagus, liver, colorectum, and female breast is causally related to alcohol consumption”. They also concluded that acetaldehyde resulting from the metabolism of ethanol contributes to malignant esophageal tumors.

WHO (2010) also concluded that there is sufficient evidence in experimental animals for the carcinogenicity of both ethanol and acetaldehyde. Their overall conclusions regarding the carcinogenicity of ethanol are based on epidemiological data indicating that cancer effects are not dependant on the type of alcoholic beverage, the information indicating ethanol causes cancer in experimental animals is sufficient, and the evidence that acetaldehyde contributes to the incidence of esophageal tumors. WHO (2010) provides an extensive discussion of possible mechanisms for ethanol-induced carcinogenicity, and concludes that the mechanisms are complex and not well characterized. They also indicated that the identification of ethanol as a carcinogenic component of alcoholic beverages does not preclude the possibility of other components contributing to carcinogenicity. Baan et al (2007) reported that in most studies where ethanol was administered in conjunction with a known carcinogen, the carcinogenic effect was enhanced.

An earlier evaluation of the carcinogenicity of ethanol (NTP 2005) also lists consumption of alcoholic beverages as *known to be a human carcinogen* based on sufficient evidence of carcinogenicity in human studies. They found consumption of alcoholic beverages as causally related to cancers of the mouth, pharynx, larynx, and esophagus. They also concluded that



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animal studies indicated that the ethanol component may not solely be responsible for cancer incidence resulting from alcohol consumption.

#### ***C4-4 Relevance of Chronic Exposure Levels to Environmental Exposures***

Spill events of ethanol generally last for a relatively short time frame (days), as described in Section 3.0 and Appendix A. The only possibility of long term or chronic exposures is from drinking water exposures, which may result from groundwater or surface water releases. However, biodegradation is expected to reduce concentrations in these media relatively rapidly. As a result, the potential for exposures of a magnitude and duration that could result in chronic effects, such as fetal alcohol syndrome and cancer, is unlikely in spill situations.

***Appendix D***  
***Draft SOP***  
***Field Hydrometer Gross Measurement of Ethanol and/or***  
***Denatured Ethanol***

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NOTE: THIS DRAFT SOP WAS DEVELOPED FROM ASTM METHOD 1250. IT HAS NOT BEEN TESTED FOR USE IN THE FIELD WITH DENATURED ETHANOL.

## **D1. INTRODUCTION**

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Hydrometers have been used for many applications to determine the specific gravity of materials, including ethanol. It is used by ATF to quickly identify the approximate concentration of ethanol.

The use of hydrometers with temperature correction for ethanol and water can provide a concentration of ethanol and water with good approximation, as long as the liquid is a mixture of ethanol and water. When other materials are also in solution, the resulting specific gravity and therefore the reading from the hydrometer will result in a reduced level of accuracy. When ethanol has been denatured, this will be the case.

It is expected that the use of a hydrometer in the field for a release situation, will provide a gross measurement of the concentration of ethanol, dependent on the level of other contaminants in the liquid.

## **D2. EQUIPMENT AND SUPPLIES**

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Depending on the chosen method, use:

- A proof hydrometer with a range from 0 to 200 proof (0-100%) and hydrometer jar.
- A thermometer with a temperature range of 0°F to 110°F
- Filter paper, funnel and 500 ml. flask.
- Recordkeeping and Documentation Supplies:
- Field logbook (w/ waterproof paper is recommended) or field forms
- Indelible pens
- Calibration and Use

### ***D3. HYDROMETER METHOD CALIBRATION***

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For purposes of having a reference material, a known high proof liquid should be used to calibrate the use of the hydrometer and thermometer using the following steps:

- Rinse the hydrometer jar with the reference liquid.
- Fill the jar with a liquid volume that will allow the hydrometer to freely float the hydrometer without overflowing when the hydrometer is placed in the liquid.
- Place the hydrometer in the liquid, letting the hydrometer settle its movement in the liquid. Record the raw reading as shown in Figure 2.
- After the hydrometer reading has been recorded, remove and place the thermometer in the liquid.
- Take the temperature reading of the liquid allowing time for the temperature reading to equilibrate. Record the temperature.
- The reading is typically adjusted for temperature, but for this gross reading, this adjustment is not necessary.

This result should be within 5 proof (2.5%) of the labeled proof of the liquid (not considering the presence of other contaminants).

### ***D4. GENERAL PROCEDURE INFORMATION***

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The hydrometers used are graduated to read the proof of aqueous alcoholic solutions at 60 degrees Fahrenheit; thus, they read, 0 for water, 100 for proof spirits, and 200 for absolute alcohol. Because of temperature-density relationships and the selection of 60 degrees Fahrenheit for reporting proof, the hydrometer readings will be less than the true percent of proof at temperatures below 60 degrees Fahrenheit and greater than the true percent of proof at temperatures above 60 degrees Fahrenheit. However, the differences are relatively small and not necessary for a gross screening.

#### ***D4-1 Field sample method***

Follow the same steps as in the calibration however, if the raw sample contains visible particulate, filtering of the sample is recommended. Use the filter paper, funnel and flask to

catch the filtered liquid. Then proceed to the steps for calibration to estimate the proof of the liquid.

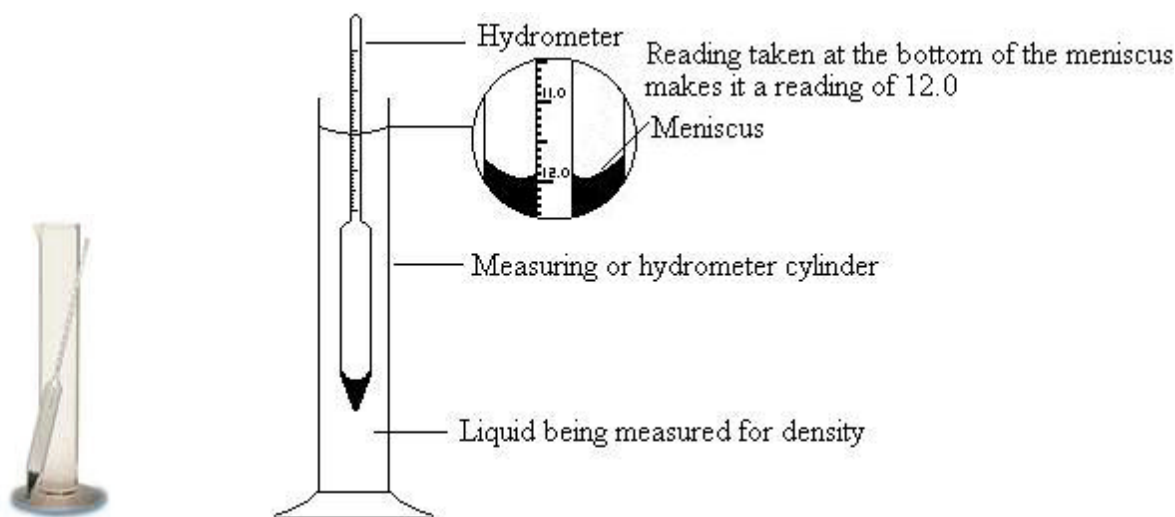


Figure 1

Figure 2

#### D4-2 General Concerns for Hydrometer Method

Care should be exercised to obtain accurate hydrometer and thermometer readings. In order to accomplish this result, the following precautions should be observed. Bulk liquids should be thoroughly agitated so that the test samples will be representative of the entire quantity. The hydrometers should be kept clean and free of any oily substance. Immediately before readings are taken, the glass cylinder containing the thermometer should be rinsed several times with the liquid which is to be gauged so as to bring both the cylinder and the thermometer to the temperature of the spirits (if time permits, it is desirable to bring both the spirits and the instruments to room temperature). If the outer surface of the cylinder becomes wet, it should be wiped dry to avoid the cooling effect of rapid evaporation. During the readings the cylinder should be protected from drafts or other conditions which might affect its temperature. The hands should not be placed on the cylinder in such a manner as to warm the liquid contained therein. The hydrometer should be inserted in the liquid and the hydrometer bulb raised and lowered 5 or 6 times to obtain an even temperature distribution over its surface.

When the ethanol has been denatured there will be a skewing of the resultant proof reading (if still in solution) because the denaturant has a different density. In the case of gasoline, the specific gravity is lower than ethanol or water, therefore the apparent proof reading will be

higher than it actually is. Because of this, realize that the proof reading could be as much as 10% lower than the reading given on a proof hydrometer.

### ***D4-3 Preventive Maintenance:***

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To ensure proper readings, it is important to keep the hydrometer and thermometer in a case after cleaning both after each use.

Any debris left on the hydrometer will result with incorrect readings. Check the condition of the hydrometer and thermometer before each use to ensure there is not breaks in the glass. If there are any cracks, the hydrometer or thermometer must be replaced.

### ***D4-4 Documentation***

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Record all field-testing measurement data, to include the following:

- Project name
- Date and time of measurement or test (including time zone, if applicable)
- Source and location of the measurement or test sample (e.g., monitoring well identification number, outfall number, station number or other description)
- Latitude and longitude of sampling source location (if required)
- Measurement or test sample value
- Temperature of sample
- Initials or name of analyst performing the measurement.